STRUCTURE OF A SHOCK WAVE IN A DISSOCIATING DIATOMIC GAS

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CERTIFICATE

This is to certify that the work *STRUCTURE OF A SHOCK WAVE IN A DISSOCIATING DIATOMIC GAS* has been carried out under my supervision and has not been submitted elsewhere for a degree.

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SYNOPSIS

A kinetic theory approach is used for investigating the structure of shock wave in a dissociating diatomic gas. An axially elastic sphero-cylinder molecular model which permits transfer of rotational and vibrational energy at a collision is proposed for a vibrationally relaxing diatomic gas. The axial elasticity has been introduced to account for the vibrational degrees of freedom. The distribution function in such a case depends on a set of 14 variables $(\underset{\sim}{x}$, $\underset{\sim}{c}$, $\underset{\sim}{e}$, $\underset{\sim}{\omega}$, where B and ϕ are required to describe the vibrational state of a molecule.

The mathematical description used for working out the collision dynamics of the axially elastic spherocylinder molecules, closely follows the one used for the rigid spherocylinders by Haight and Lundgre The geometry and dynamics of a collision between two molecules are studi at first.

The frequency of binary collisions in the diatomic gas is obtained. This is used in writing down the collision integral in the Boltzmann equation. For the Boltzmann equation, thus formulated, an H-Theorem is given and through this theorem, the equilibrium solution of the Boltzman equation is obtained.

For the shock structure- problem, a trimodal and a quadrimodal ansatz are proposed and a moment method is used to find the   wn

vibrational energy are used in addition to the conservation equations.
For the quadrimodal approach, the rotational energy, vibrational energy
and the c_x^2 moment of the Boltzmann equation are used to determine the
weight functions again, in addition to the conservation equations. The
collision integrals in these moment equations are 22 fold out of which
16 fold integrations are carried out analytically and the remaining
integrations were performed numerically using the Monte Carlo technique.
The set of equations in the unknown weight functions have been solved
numerically to get the shock profiles for a range of Mach numbers and
upstream pressures for nitrogen gas.

Further, for the case of a dissociating gas the Boltzmann equation
is modified by including the collision terms representing dissociative
and recombinative collisions. A separate Boltzmann equation is written
for the atom species present in the dissociating diatomic gas. These
two Boltzmann equations are solved using a moment method for the shock
boundary conditions. The trimodal ansatz suggested earlier is used for
the diatomic molecular distribution function and a bimodal distribution
function for atom species.

In addition to the two species conservation equations, the
rotational and vibrational energy equations have been used for deter-
mining the weight functions. Again the collision integrals in these
moment equations are also 22 fold and have been evaluated as in the
earlier case. The shock profiles have been obtained by solving the set
of equations in the weight functions for various Mach number and upstre
pressures for nitrogen gas.

CONTENTS

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List of Principal Symbols

a : Radius of the hemispheres in the sphero-cylinder molecule

b : Distance between the two centres of the hemispheres constituting the sphero-cylinder molecule.

B : Amplitude of vibration of the diatomic molecule

$\underset{\sim}{c}$: Velocity of the centre of mass of the molecule in the laboratory co-ordinate system.

c_x, c_y, c_z : Components of $\underset{\sim}{c}$ in the cartesian co-ordinate system.

D : Dissociation energy of a molecule

$\underset{\sim}{e}$: Unit vector along the axis of the molecule

f : Distribution function for molecules

F : Distribution function for atom

$\underset{\sim}{F}$: Force per unit mass of the molecule

$\underset{\bullet}{g}$: Relative velocity of the point of contact on molecule 2 with respect to the point of contact on the molecule 1 just before the collision.

G : Gain term in the collision integral

I : Impulse transmitted at a collision by molecule 1 to molecule 2; also integral.

J_1 : Moment of inertia of the molecule about an axis perpendicular to the axis of the molecule.

J_2 : Moment of inertia of the molecule about its own axis.

$\bar{J}$: Collision integral in the Boltzmann equation for molecules.

$\underset{\sim}{J}$:   Moment of inertia tensor of the molecule

k_d :   Dissociation rate constant.

k_r .   Recombination rate constant.

K :   Function which defines differential collision cross section.

$K(T)$:   Equilibrium constant

L :   Loss term in the collision integral.

L^* :   Characteristic length used for non-dimensionalising shock thickness by Robben and Talbot (1966)

m :   Mass of the molecule

n :   Number density of molecules

n_o :   Number density of atoms

$\underset{\sim}{n}$:   Unit vector normal to the surface of the molecule

N :   Number of Trials in the Monte Carlo integration; also an integer

p_1 :   Upstream pressure

P_o, P_1 :   Steric factors for intermolecular collisions and molecule-atom collisions respectively.

$\underset{\sim}{r}$:   Distance vector from the centre of mass of a molecule to a point on the surface of the molecule.

$\underset{\sim}{R}$:   Distance vector from the centre of mass of molecule 1 to the centre of mass of molecule 2 at the instant of collision.

s :   Spring constant for the molecule

s_o, s_1 :   Parameters characterising the degree of participation of internal degrees of freedom for intermolecular and molecule-atom collisions respectively.

S	:	Interaction surface
t	:	Time
T	:	Temperature
T_1	:	Upstream temperature
$\bar{T}$	:	Non-dimensional temperature
$\underset{\sim}{u}$	:	Macroscopic velocity of gas
$\underset{\sim}{U}$	:	Unit tensor
$\underset{\sim}{W}_i$	:	Weight functions
x	:	Distance across the shock
$\underset{\sim}{x}$	:	Location vector of a molecule
α	:	Degree of Dissociation
$\bar{\alpha}$	:	Nondimensional degree of dissociation
Δ	:	Nondimensional shock thickness
ϕ	:	Phase angle for the simple harmonic vibrations of a molecule
λ_1	:	Mean free path for the gas upstream (equivalent rigid sphere model)
ν	:	Frequency of vibrations of a molecule
ξ, ξ^*	:	Nondimensional distance across the shock.
$\underset{\sim}{\omega}$	:	Angular velocity of a molecule
$\omega_1, \omega_2, \omega_3$	:	Components of $\underset{\sim}{\omega}$ in the cartesian co-ordinate system
$\omega_{\parallel}$	:	Component of $\underset{\sim}{\omega}$ along the axis of the molecule
$\omega_\perp$	:	Component of $\underset{\sim}{\omega}$ perpendicular to the axis of the molecule
τ	:	Relaxation time; also volume.
ρ	:	Density

ρ Non-dimensional density

Subscripts

r	:	Rotational (for T, $\bar{T}$ and τ)
t	:	Translational (for T, $\bar{T}$ and τ)
v	:	Vibrational (for T, $\bar{T}$ and τ)
R	:	Rotational (for Δ)
T	:	Translational (for Δ)
V	:	Vibrational (for Δ)
eN	:	Monte Carlo estimate for the integral with N trials (for I and S_o).

INTRODUCTION

1.1.   This work is concerned with the problem of shock structure
in a dissociating diatomic gas.   In gas dynamics, it is customary
to assume the shock to be a surface of discontinuity across which
two uniform states exist.   These two uniform states are related
by the Rankine - Hugoniot relations.   However, to describe the
narrow transition zone in the shock wave it is necessary to consider
the effects of viscosity and thermal conductivity.   This problem
was solved within the frame work of the Navier-Stokes equations
for a monatomic gas first by Taylor (1910) and later by Becker
(1921), Thomas (1944) and others.   The thickness of shock wave
was found to be of the order of a few mean free paths of the gas
upstream.   But the validity of the Navier-Stokes equations for
the shock phenomenon is questionable as the characteristic length *for*
for the shock is so small as to break the continuum hypothesis
made in the formulation of these equations.   The results obtained
by continuum and kinetic theory approaches for the shock problem,
as given by Gilbarg and Paolucci (1953), show roughly equivalent
shock thicknesses.   However, the merit of a theory should be
judged by comparison of its results with those given by experiments.
Observations made for monatomic gases by Talbot (1962) and
Sherman and Talbot (1960), after a careful study of the available

data, both experimental and theoretical, show that the Navier-Stokes equations yield sufficiently good results for weak shocks $(M < 2)$; but for strong shocks, $(M > 2)$, these results are not satisfactory.

To overcome this, Mott-Smith (1951) treated the problem for the strong shock case, from the molecular point of view by using moments of the Boltzmann equation. He proposed an ansatz for the distribution function considering the physics of the problem. The shock region being a thin one, he suggested that molecules from both the hot and the cold side might freely interpenetrate into this region. He assumed the distribution function to be a weight sum of two Maxwellians, one corresponding to the cold side and the other to the hot. The two weight functions were determined approximately by satisfying the Boltzmann equation in an average sense (moment method). The results obtained thus were found to b satisfactory for a strong shock. Mott-Smith's analysis was, however, restricted to rigid sphere and Sutherland molecules. It was further extended to a general inter-molecular inverse-power repulsive force law by Muckenfuss (1960).

For the case of a diatomic gas with rotational degrees of freedom the shock problem was solved by Talbot and Scala (1961) from a continuum point of view (modified Navier-Stokes equations). They defined two temperatures separately one for translational degrees and the other for rotational ones and incorporated them in the Navier-Stokes equations. For small relaxation times they proposed a perturbation technique based on a modified bulk viscosi

whereas for long relaxation times they used a subsidiary relaxation equation to complete the set of equations. The results obtained by the bulk viscosity approach were found to be unsatisfactory. Nevertheless, the relaxation model was found to give phenomenologically acceptable results which depend on the relaxation time in addition to the Mach number. Just as in the monatomic case, in this case also, it is reasonable to expect the continuum analysis yield results valid for weak shocks only. Thus the results given by the relaxation model are limited to weak shock cases only.

Scala and Talbot (1963) further extended the two temperature relaxation model to a vibrationally relaxing diatomic gas by defining one more temperature to include vibrational relaxation effects. They also used in this case, two subsidiary relaxation equations, instead of one, to complete the set of equations. With these modifications the Navier-Stokes equations were solved along with the two relaxation equations for the shock problem. Out of the two relaxation times, they fixed one, the rotational relaxation time, and obtained results for different vibrational relaxation times and for two Mach numbers. In this analysis also physically acceptable solutions were obtained but the limitation of such a (continuum) theory, as mentioned earlier, lies in the fact that it is capable of predicting the structure of only weak shock waves satisfactorily.

Turcotte and Scholnick (1969) proposed a Beam Continuum Mod. (B.C.M.) for monatomic strong shocks in hypersonic flows. In this the upstream hypersonic flow is taken to be a zero temperature

...~~roach, the classical descrip-

continuum flow is assumed to take place.

Further, this change is supposed to be brought about by a single
collision per molecule of the beam.   The Navier-Stokes equations
are used to treat the continuum particles with additional terms to
account for the addition of mass, momentum and energy from beam
particles.   The shock profile given by this theory is in reasonable
agreement with some of the experimental profiles given by Camac
(1965) and Robben and Talbot (1966). - ...

This model (B.C.M.) has been later extended by Turcotte (1969)
to the diatomic case (to include the effects of rotational degrees
of freedom).   The modified Navier-Stokes equations proposed by
Talbot and Scala (1961) have been used to treat the continuum flow
in this case.   An equivalent hard sphere model was used to specify
the interaction cross section which appears in the expressions for
the transport coefficients.   The results were obtained by varying
the number of collisions required for rotational relaxation, as a
parameter for two different Mach numbers.   They are in good agreemen
with the experimental results given for strong shocks in nitrogen,
by Robben and Talbot (1966).

1.2.   Before dealing with the shock problem in a diatomic gas from
a molecular point of view, one has to develop a suitable kinetic
theory which takes into account the internal degrees of freedom.
There are two available approaches to the kinetic theory of diatomic
gases - the semi-quantum mechanical and the classical.

In the semi-quantum mechanical approach, the classical description for the translational degrees of freedom is retained, but the internal degrees of freedom are handled quantum mechanically. The difficulties in such a treatment lie in the quantum mechanical evaluation of angular dependent in-elastic cross sections. This theory was given by Wang Chang and Uhlenbeck (1951) and later was used by Monchik, Yun and Mason (1963) for evaluating the transport properties of gases. To enable a treatment of a wider class of problems in gas dynamics, physically plausible kinetic models were proposed for a modified Boltzmann equation, by Morse (1964), Brau (1967) and Hanson and Morse (1967). These are similar in spirit to the B.G.K. model (1954) for the monatomic gas case.

Further, an analysis close to Grad's thirteen moment approximation (1949) for the monatomic gas case has been given by Mc Cormic (1968) to get a set of kinetic equations for poly-atomic gases. He used Wang Chang, Uhlenbeck and de Boer equation (1964) (inelastic Boltzmann equation) and four additional moments to take care of the internal temperature and the internal heat-flux vector to obtain the seventeen moment approximation. These equations are used for studying the near equilibrium and relaxation type of flow. The results obtained are in very close agreement with those of Wang Chan et al (1964) analysis.

In the classical approach a suitable model is chosen for the gas molecule possessing internal degrees of freedom. The two body collision problem is solved classically and a modified Boltzman equation formulated. Such a theory was developed by Curtiss (1956, 1957) for diatomic gases having rotational degrees of freedom, and

was further used for evaluating the transport properties for gases with loaded sphere and sphero-cylinder molecular models by Dalher and Sather (1963) and Sandler (1966, 1968).

1.3.   The first attempt to obtain the shock structure in a rotationally relaxing gas from the molecular point of view was made by Haight and Lundgren (1965, 1967, 1968).   They used the kinetic theory developed by a classical approach, for the strong shock.   A trimodal distribution function, built up using three Maxwellians, describing the two uniform states - the upstream and the down stree and an intermediate state having no rotational excitation - was proposed.   A moment method was used to determine the three weight functions.   This analysis is an extension of Mott-Smith's bimodal theory (1951).   Shock profiles for three different cases of molecular models (rough sphere, loaded sphere and sphero-cylinder) were obtained.   As a special case of this theory, it was possible to recover Mott-Smith monatomic results.

Later the trimodal ansatz was used by Brau, Simons and Macon (1969) in solving the kinetic model equation proposed by Brau (196⁷ with the shock boundary conditions.   They also tried an alternate ansatz based on a model developed by Anderson and Macomber (1965) for monatomic gases.   While the trimodal theory gave good results for both low and high upstream Mach numbers agreeing with the experimental data of Robben and Talbot (1966) for shock profiles ar shock thickness, the second ansatz yielded reasonably good results only for shock thickness.   The shock profiles predicted by the sec ansatz were not in agreement with the experimental shock profiles :

high upstream Mach numbers.

Venkatraman and Morse (1969) used the kinetic model given by
Morse (1964), to study the structure of a shock wave in diatomic
gases with rotational degrees of freedom. They assumed a suitably
modified Mott-Smith bimodal distribution. In this ansatz, in additio[n]
to the two weight functions, the parameters of the second Maxwellian
were also taken to be functions of the distance. This was necessary
in order to satisfy the energy relaxation equation. The three
conservation equations and two moment equations (c_x^2 and $1/2 \, mc^2 - E_1$)
were used to determine the five unknowns in the problem. Comparison
of density and temperature profiles with the experimental data of
Robben and Talbot (1966) is quite good.

Recently Machperson (1971) followed the classical approach
and a Monte Carlo scheme for obtaining the rotational temperature
profiles for shock waves in oxygen and nitrogen. He also calculated
the variation of translational temperature and density inside the
shock. The intermolecular potential used in this analysis is the
one given by Parker (1959). The shock thicknesses predicted thus,
compare well with the experimental values obtained by Marrone (1967).

Venkataraman and Morse (1970) extended their earlier analysis
(1969) to predict the effects of vibrational relaxation on the
shock structure in diatomic gas. A kinetic model, similar to the
one given by Morse (1964), with additional terms to include vibration[al]
effects, was also proposed by them. In addition to the three
conservation equations, they used c_x^2, ($\frac{1}{2} \, mc^2 - E_{R1} - E_{v1}$) moments of
the kinetic equation. Shock structures in oxygen, nitrogen and

carbon di-oxide were obtained for high Mach numbers using this model.

1.4.   In the present work, an axially elastic sphero-cylinder model is proposed for a diatomic gas molecule.   Axial elasticity has been introduced to account for the vibrational degrees of freedom.   The distribution function in such a case depends on $\underset{\sim}{x}$, $\underset{\sim}{c}$, $\underset{\sim}{e}$, $\underset{\sim}{\omega}$, B and ϕ .   The last two of the variables are required to describe the vibrational state of a molecule.   A mathematical description of the molecule is required for working out the dynamics of a collision between two molecules.   The mathematical representation followed for the axially elastic vibrating molecule follows closely, the one used by Haight and Lundgren (1965, 1967, 1968) for the rigid non-central particles.

The geometry and dynamics of a collision between two molecules are studied at first.   The collision integrals in the modified Boltz equation are formulated.   The moment equation corresponding to the Maxwell transfer equation **is** obtained.   As special cases of this, th three conservation equations are written down.   Through an H-theorem the corresponding equilibrium distribution is obtained.

Further for investigating the shock structure in a vibrationall and rotationally relaxing diatomic gas, the moment method is used. Following Mott-Smith (1951) and Haight (1965) two multi-modal ansatz for the distribution function have been proposed - the first one a tri using three Maxwellians, the second one, a quadrimodal using four Maxwellians.   In the trimodal case a molecule inside the shock is assumed to belong either to the upstream equilibrium state, the

downstream . Maxwellian state or an intermediate equilibrium state without vibrational excitations. In the quadrimodal case, in addition to these three Maxwellians, another Maxwellian, which corresponds to an intermediate equilibrium state with only translation degrees of freedom fully excited and rotational and vibrational degrees of freedom frozen, is taken. The three conservation equation effectively give one algebraic equation in the unknown weight functions. To determine three weight functions in the trimodal formulation, two moment equations - rotational energy and vibrational energy - are used. For the quadrimodal approach the fourth equation used is c_x^2 moment of the Boltzmann equation. The collision integral in these moment equations are 22 fold, out of which 16 fold integrations are carried out analytically and the remaining integrations were done numerically using the Monte Carlo technique. Effectively we obtain a set of two non-linear, first order, coupled total differential equations and an algebraic equation in the three unknown weight functions for the trimodal case whereas for the quadrimodal case an additional differential equation is provided by the c_x^2 moment equation. These equations are solved numerically on a computer and shock profiles are obtained for various Mach numbers and upstream pressures for nitrogen.

1.5. As the Mach number increases the degree of dissociation in a diatomic gas behind the shock wave becomes increasingly larger. Thus the theory proposed above for the shock structure is valid at or moderately high Mach numbers and it is necessary to include the effec of dissociation in the analysis of the shock structure at higher Mach numbers.

The analysis outlined above has to be modified in two ways: firstly because of the appearance of a second species, the atom, due to the onset of molecular dissociation, an additional Boltzmann equation has to be introduced governing the distribution function of the atom species; secondly, additional collisional terms appear on the right hand side of the Boltzmann equation for the diatomic species representing dissociative and recombinative collisions corresponding to atom – molecule collisions. Thus the problem reduces to the calculation of the shock structure in a chemically reacting mixture of two species, atoms and molecules. In this case also, a moment method is used to solve the Boltzmann equations for two species. The trimodal ansatz suggested earlier is adopted for the diatomic species and the Mott-Smith bimodal distribution is used for the atom species. Two species conservation equations and two moments of the Boltzmann equation for diatomic species (rotational energy and vibrational energy) are used to determine the unknown weight functions. The shock profiles are obtained for a range of upstream Mach numbers and upstream pressures in nitrogen.

In Chapter 2 the collision dynamics of two vibrating molecules is solved. In Chapter 3 is given the formulation of Boltzmann equati for a diatomic gas and also the equilibrium solution for this equatic The trimodal and quadrimodal analysis for the structure of a shock wave in a vibrationally relaxing diatomic gas has been dealt in Chapter 4. The dissociation and recombination rates are written for intermolecular and molecule-atom collisions in Chapter 5. In this chapter, the formulation for the shock structure problem considering

the dissociation effects is also given. In Chapter 6 is discussed the numerical technique (Monte Carlo method) used for evaluating the multiple integrals in the moment equations along with the error estimates. Finally in Chapter 7 are given results and conclusions of the present investigations.

CHAPTER — 2

COLLISION DYNAMICS

2.1. Molecular Model :

Before developing a kinetic theory for a vibrationally, rotationally and translationally relaxing gas, a suitable molecular model has to be postulated. Jeans (1925), proposed a rigid loaded sphere model for rotationally relaxing diatomic gas molecules. Later, Hirschfelder, Curtiss and Bird (1954) introduced a rigid spherocylinder model in the kinetic theory of diatomic gases. However, one of the first few attempts in developing a kinetic theory of non-spherical molecules, with rotational degrees of freedom by Curtiss (1956), used a general class of molecules which are rigid convex bodies of revolution. The loaded sphere model is a special case of this general model and the spherocylinder, in some sense, also belongs to the general class of convex bodies of revolution.

With the available models the effects of rotational relaxation on transport properties in a diatomic gas, have been estimated by Sather (1963) and Sandler (1966,1968) and on the shock structure by Haight (1965) in such a gas. A classical theory of vibrationally relaxing diatomic gas is not available, so far in the literature. For this purpose, a molecular model which permits the transfer of vibrational energy in addition to the rotational and translational energies at a collision has to be chosen at first.

In this thesis an axially elastic sphero-cylinder model is proposed for such a gas. The axial elasticity is introduced for the central cylindrical portion to allow the molecules vibrational degrees of freedom. This model can be regarded as composed of an assembly of two rigid spherical atoms connected by a linear elastic spring guided in a rigid hollow cylindrical shell as shown in Fig.(2.1.1).

The vibrational degrees, as indicated earlier are treated classi The justification for this is given in Chapter 3. The molecule is assumed to vibrate from an initial equilibrium state. The amplitude of the axial vibration is taken to be small compared to the equilibriur separation distance between the two atoms constituting the molecule. The molecule is assumed to be rigid in the transverse direction, so as not to excite any bending vibrations in that direction. For a given homogeneous species of molecules the frequency of vibrations of a molecule is the same for all the molecules. However, the two variabl used to describe the vibrational state of a molecule are: the maximum amplitude, B, of vibration measured from the equilibrium positions of two atoms and the phase angle, ϕ , of the simple harmonic vibrations of an individual molecule. The amplitude B is a measure of the vibra tional energy of a molecule.

In addition to the mass and the two geometrical parameters (a and b) required to specify a rigid sphero-cylinder model, the axially elastic spherocylinder model also needs a spring constant, s, for its complete description. As the analysis is restricted to small amplitum of vibration, a linear spring is an adequate representation. The two

variables B and ϕ , describing the vibrational state of a molecule enter
not only in the analysis of collision dynamics, but also in the
definition of a distribution function for the gas. The important
physical constants for some diatomic molecules are shown in Table
(2.1.1).

2.2. Surface Representation :

The molecular surface is described in terms of a unit vector
$\underset{\sim}{e}$ along the longitudinal axis of the molecule and a unit vector $\underset{\sim}{n}$
normal to the surface, such that the location vector $\underset{\sim}{r}$ for a point
on the surface from the centre of mass of the molecule may be written
as follows (See Fig. 2.2.1.) :

$$\underset{\sim}{r} = \{b + B \cos (\nu t + \phi)\} \, \underset{\sim}{e} + a \, \underset{\sim}{n} \Big\} \quad \text{for points on the}$$
$$\underset{\sim}{r} \cdot \underset{\sim}{n} = \{b + B \cos (\nu t + \phi)\} \, \underset{\sim}{e} \cdot \underset{\sim}{n} + a \Big) \quad \text{positive } \underset{\sim}{e} \text{ hemisphere}$$

$$\underset{\sim}{r} = - \{b + B \cos (\nu t + \phi)\} \, \underset{\sim}{e} + a \, \underset{\sim}{n} \Big] \quad \text{for points on the}$$
$$\underset{\sim}{r} \cdot \underset{\sim}{n} = - \{b + B \cos (\nu t + \phi)\} \, \underset{\sim}{e} \cdot \underset{\sim}{n} + a \Big) \quad \text{negative } \underset{\sim}{e} \text{ hemisphere}$$

$$\underset{\sim}{r} \cdot \underset{\sim}{n} = a \ , \quad \underset{\sim}{e} \cdot \underset{\sim}{n} = 0 \qquad \text{for points on the cylindrical}$$
surface

(2.2.1)

2.3. Dynamics of a Two Body Collision :

In deriving the Boltzmann equation, we shall consider a dilute
gas and neglect the effects of ternery and higher order collisions,
as in the case of a monatomic gas. Thus we need solve only a binary
collision problem. The collisional contact time for vibrating
molecules is finite and is appreciably large compared to the period of
vibration (Stupochenko, 1966) . However, in this analysis we assume

TABLE 2.1.1

Molecule	H_2	N_2	O_2
Atomic mass number	1	14	16
Inter-atomic distance $re(\overset{\circ}{A})$	0.7416	1.094	1.2074
Dissociation Energy $D(eV)$	4.476	9.74	5.11
Dissociation Temperature $= D/k(°K)$	-	113000	59380
Characteristic Vibration temperature $= h\nu/k(°K)$	5910	3340	2230
Characteristic rotation temperature $(°K)$	85.4	2.9	2.1
a/b	3.8	3.1*	-
$\dfrac{mb^2}{2J_1}$	-	0.025*	-

* Calculations are made for $a/b = 3$ and $\dfrac{mb^2}{2J_1} = 1/32$ and these are

close to recommended values for nitrogen molecules by Haight.

the collisions to be instantaneous. At a collision an impulse I is transmitted from molecule 1 to molecule 2 in the direction of the common normal $\underset{\sim}{n}$ at the point of contact (Fig. 2.3.1). The line of action of the impulse does not always pass through the centres of mass of the molecules. Thus, in addition to the transfer of linear impulse, an angular impulse is also transmitted at a collision. Further, the simple harmonic oscillations absorb some energy due to the impulse. From the conservation of linear momentum we have,

$$\underset{\sim}{c}_1' = \underset{\sim}{c}_1 - \frac{I\underset{\sim}{n}}{m_1} \qquad \text{for molecule 1}$$

$$\underset{\sim}{c}_2' = \underset{\sim}{c}_2 + \frac{I\underset{\sim}{n}}{m_2} \qquad \text{for molecule 2} \qquad (2.3.1)$$

The angular momentum conservation gives us

$$\underset{\sim}{\omega}_1' = \underset{\sim}{\omega}_1 - \underset{\sim}{J}_1^{-1} \cdot I\underset{\sim}{n} \times \underset{\sim}{r}_1$$

$$\underset{\sim}{\omega}_2' = \underset{\sim}{\omega}_2 + \underset{\sim}{J}_2^{-1} \cdot I\underset{\sim}{n} \times \underset{\sim}{r}_2 \qquad (2.3.2)$$

The energy absorbed by the vibrational degrees of freedom for molecule 1 and 2 may be written as

$$(\Delta V.E.)_1 = - (I\ \underset{\sim}{n}) \cdot (\underset{\sim}{e}_1\ \nu\ B_1\ \sin\ \phi_1)$$

$$(\Delta V.E.)_2 = (I\ \underset{\sim}{n}) \cdot (\underset{\sim}{e}_2\ \nu\ B_2\ \sin\ \phi_2) \qquad (2.3.3)$$

Finally we have from the conservation of energy,

$$\{\tfrac{1}{2}\,m_1\underset{\sim}{c}_1^2 + \tfrac{1}{2}\,\underset{\sim}{\omega}_1\underset{\sim}{J}_1\,\underset{\sim}{\omega}_1 + \tfrac{1}{2}\,s(2B_1)^2\} + \{\tfrac{1}{2}\,m_2\,\underset{\sim}{c}_2^2 + \tfrac{1}{2}\,\underset{\sim}{\omega}_2 \cdot \underset{\sim}{J}_2 \cdot \underset{\sim}{\omega}_2$$

$$+ \tfrac{1}{2}\,s(2B_2)^2\} = \{\tfrac{1}{2}\,m_1\,\underset{\sim}{c}_1'^2 + \tfrac{1}{2}\,\underset{\sim}{\omega}_1' \cdot \underset{\sim}{J}_1 \cdot \underset{\sim}{\omega}_1' + \tfrac{1}{2}\,s(2B_1)^2 + (\Delta VE)$$

$$+ \{\tfrac{1}{2}\,m_2\,\underset{\sim}{c}_2^2 + \tfrac{1}{2}\,\underset{\sim}{\omega}_2' \cdot \underset{\sim}{J}_2 \cdot \underset{\sim}{\omega}_2' + \tfrac{1}{2}\,s(2B_2)^2 + (\Delta VE)_2\} \qquad (2.3$$

¯‌ɪ in a tensor. In product it acts as a scalar

Substituting from Eqns. (2.3.1.) to (2.3.3.) in Eqn. (2.3.4.), we have for the impulse I :

$$I = (- \underset{\sim}{g} \cdot \underset{\sim}{n})/\{\frac{1}{2} (\frac{1}{m_1} + \frac{1}{m_2}) + \frac{(\underset{\sim}{r_1} \times \underset{\sim}{n})^2}{2 J_{11}} + \frac{(\underset{\sim}{r_2} \times \underset{\sim}{n})^2}{2 J_{12}}\} \qquad (2.3.5)$$

where

$$\underset{\sim}{g} = (\underset{\sim}{c_2} + \underset{\sim}{\omega_2} \times \underset{\sim}{r_2} - \underset{\sim}{e_2} B_2 \nu \sin \phi_2)$$

$$(2.3.6)$$

$$- (\underset{\sim}{c_1} + \underset{\sim}{\omega_1} \times \underset{\sim}{r_1} - \underset{\sim}{e_1} B_1 \nu \sin \phi_1)$$

Once I is known in terms of the pre-collision variables and the collision geometry, the post collision variables can be determined from the Eqns. (2.3.1.) to (2.3.3.). Thus binary collision problem is completely solved for vibrating molecules.

In the formulation of Boltzmann equation for dissociating diatomic gas (see Chapter 5), we need to consider the collisions between an atom and a molecule. The post collision variables for such a collision can be obtained as a special case of the above by putting for particle 2 (atom)

$$m_2 = \frac{m_1}{2} \; , \; B_2 = 0, \; \phi_2 = 0, \; \text{and} \; \underset{\sim}{\omega_2} = 0 \qquad (2.3.7)$$

In Chapter 3, a Boltzmann equation for a diatomic gas consisting of elastic spherocylinder molecules is formulated and an equilibrium solution is obtained for this equation.

CHAPTER - 3

BOLTZMANN EQUATION AND THE H-THEOREM

3.1. Introduction - In this chapter a kinetic theory of vibrationally relaxing diatomic gas is given. As the end result of this thesis is not kinetic theory per se , a less general view is taken in formulating the Boltzmann equation. This is especially so in treating the vibrational degrees of freedom classically. Strictly speaking, the vibrational degrees of freedom exhibit quantum behaviour and the vibrational energy of N identical oscillators (diatomic molecules) is given by Planck's function:

$$E_{vib} = NkT \left\{ \frac{h\nu/kT}{e^{h\nu/kT} - 1} \right\} \qquad (3.1.1)$$

where ν is the frequency of vibration and T is the translational temperature of the gas. In the limit $kT >> h\nu$ the vibrational energy approaches its classical value $E_{vib} = NkT$. Actually the energy is already close to its classical value, when $kT \sim h\nu$. Thus, for example, at $kT/h\nu = 0.5$, we find $E_{vib} = 0.724$ NkT; at $kT/h\nu = 1$, we find $E_{vib} = 0.928$ NkT; at $kT/h\nu = 2$, we find $E_{vib} = 0.979$ NkT.

The value of $h\nu/k$ for oxygen is $2230°K$ and for nitrogen is $3340°K$. (See Table 2.1.1.).

For a shock wave in a diatomic gas there exists a narrow region (translational shock) in which vibrational excitations are practically frozen and at the tail of this region the value of $kT/h\nu > 1$.

Therefore, over a significant portion of the shock, following the translational shock, the vibrational degrees behave almost classically. Hence in the kinetic theory developed here, all the degrees of freedom including the vibrational ones are treated classically.

3.2. Boltzmann Equation -

To describe the dynamic state of an axially elastic spherocylinder molecule, a set of 13 coordinates is required.

The set consists of :

$\underline{x}$ — the physical co-ordinates of the centre of mass of the molecule

$\underline{c}$ — the translational velocity of the centre of mass of the molecule with respect to the laboratory co-ordinate system

$\underline{e}$ — the unit vector along the axis of the molecule to fix the orientation

$\underline{\omega}$ — the angular velocity of the molecule with respect to the laboratory co-ordinate system.

B — the maximum amplitude of vibration

ϕ — the phase angle of the simple harmonic oscillations of the two atoms constituting the molecule.

Thus for a gas made up of such molecules, the distribution function is a function varying in the hyper-space $\underline{q}$, t where q denotes the space defined by $(\underline{x}, \underline{c}, \underline{e}, \underline{\omega}, B, \phi)$. The probable number of molecules with their phase coordinates between $\underline{q}$ and $\underline{q} + d\underline{q}$ at any time t , is given by

$$f(\underline{q};t) \; d\underline{q}$$

or

$$f(\underset{\sim}{x},\underset{\sim}{c},\underset{\sim}{e},\underset{\sim}{\omega},\beta,\phi;t)d\underset{\sim}{x}\ d\underset{\sim}{c}\ d\underset{\sim}{e}\ d\underset{\sim}{\omega}\ d\beta\ d\phi$$

where f is the distribution function describing the state of the gas and

$$d\underset{\sim}{x} = dx\ dy\ dz\ ;\ d\underset{\sim}{c} = dc_x\ dc_y\ dc_z$$

$$d\underset{\sim}{e} = \sin\beta\ d\beta\ d\varepsilon\ ;\ d\underset{\sim}{\omega} = d\omega_1\ d\omega_2\ d\omega_3\ . \tag{3.2.1}$$

Thus the number density of the molecules at a point $\underset{\sim}{x}$ in the physical space and at a given instant t is given by the normalisation relationship:

$$n(\underset{\sim}{x},t) = \int f(\underset{\sim}{x},\underset{\sim}{c},\underset{\sim}{e},\underset{\sim}{\omega},\beta,\phi;t)\ d\underset{\sim}{x}\ d\underset{\sim}{c}\ d\underset{\sim}{e}\ d\underset{\sim}{\omega}\ d\beta\ d\phi \tag{3.2.2}$$

The variation of f with time t, is now studied to obtain a governing equation for f . In the absence of collisional effects, the time derivatives $\overset{\bullet}{\underset{\sim}{q}}$, of the 13 phase coordinates of a molecule are functions of the coordinates themselves. After an interval of time dt from the instant t, a free molecule initially having $\underset{\sim}{q}$ as its co-ordinate will occupy a point $\underset{\sim}{q} + \overset{\bullet}{\underset{\sim}{q}}\ dt$ in the hyper-space. Now consider a set of molecules in a phase volume $d\underset{\sim}{q}$ at time t around a point $\underset{\sim}{q}$. At time $t + dt$ the same molecules will be present in a phase volume $d\underset{\sim}{q}'$ around the point $\underset{\sim}{q} + \overset{\bullet}{\underset{\sim}{q}}\ dt$, if they suffer no collisions during the interval dt. However due to collisional effects, a fraction of the total number of molecules in $d\underset{\sim}{q}$, fail to reach $d\underset{\sim}{q}'$ while some molecules which were not present in $d\underset{\sim}{q}$ at time t, manage to reach $d\underset{\sim}{q}'$. The total number of particles in $d\underset{\sim}{q}'$, at time $t+dt$, is related to the number in $d\underset{\sim}{q}$ at t by the following equation.

$$f(\underset{\sim}{q}+\overset{\cdot}{\underset{\sim}{q}}\,dt;t+dt)dq' = f(\underset{\sim}{q};t)d\underset{\sim}{q} + \{G-L\}\,d\underset{\sim}{q}\,dt \tag{3.2.3}$$

where the phase volume $d\underset{\sim}{q}'$ at $\underset{\sim}{q} + \overset{\cdot}{\underset{\sim}{q}}\,dt$, $t + dt$ is related to $d\underset{\sim}{q}$ at $(\underset{\sim}{q}\ ,\ t)$ by

$$d\underset{\sim}{q}' = J_0\left\{\begin{matrix} \underset{\sim}{q} + \overset{\cdot}{\underset{\sim}{q}}\,dt \\[6pt] \underset{\sim}{q} \end{matrix}\right\} d\underset{\sim}{q} \tag{3.2.4}$$

where J_0 is the Jacobian. $G\,d\underset{\sim}{q}\,dt$ is the number of molecules reaching $d\underset{\sim}{q}'$ during dt from outside $d\underset{\sim}{q}$, or the number of molecules 'gained' by $d\underset{\sim}{q}'$ due to collisions; and $L\,d\underset{\sim}{q}\,dt$ is the number of molecules in $d\underset{\sim}{q}$ failing to reach $d\underset{\sim}{q}'$ during dt, or the number of molecules 'lost' due to collisions.   Thus, we have (by expanding the left hand side and cancelling the phase volume term on either side)

$$\frac{\partial f}{\partial t} + \frac{\partial \overset{\circ}{q}_p f}{\partial q_p} = G - L \tag{3.2.5}$$

The following are the equations of motion of a free molecule:

$$\begin{aligned} \overset{\cdot}{\underset{\sim}{x}} &= \underset{\sim}{c} \\ \overset{\cdot}{\underset{\sim}{c}} &= \underset{\sim}{F} \ ; && \text{the force per unit mass} \\ \overset{\cdot}{\underset{\sim}{e}} &= \underset{\sim}{\omega} \times \underset{\sim}{e} \end{aligned} \tag{3.2.6}$$

$$\frac{d}{dt}\,(\underset{\approx}{J}\cdot\underset{\sim}{\omega}) = \overset{\cdot}{\underset{\approx}{J}}\cdot\underset{\sim}{\omega} + \underset{\approx}{J}\cdot\overset{\cdot}{\underset{\sim}{\omega}} = 0$$

From the last equation we have

$$\overset{\cdot}{\underset{\sim}{\omega}} = \underset{\approx}{J}^{-1}\cdot\overset{\cdot}{\underset{\approx}{J}}\cdot\underset{\sim}{\omega}$$

where

$$\underset{\approx}{J} = \frac{1}{J_1}\,\underset{\approx}{U} + \left(\frac{1}{J_2} - \frac{1}{J_1}\right)\underset{\sim}{e}\,\underset{\sim}{e}$$

so that

$$\dot{\underset{\sim}{\omega}} = - \frac{J_2 - J_1}{J_1} (\underset{\sim}{\omega} \cdot \underset{\sim}{e}) \underset{\sim}{\omega} \times \underset{\sim}{e} \tag{3.2.7}$$

Substituting the above results for $\dot{q}_p$ in Eqn. $(3.2.5)$ we get

$$\frac{\partial f}{\partial t} + \underset{\sim}{c} \cdot \frac{\partial f}{\partial \underset{\sim}{x}} + \underset{\sim}{F} \cdot \frac{\partial f}{\partial \underset{\sim}{c}} + \frac{\partial}{\partial \underset{\sim}{\omega}} \cdot \{\frac{J_1 - J_2}{J_1}(\underset{\sim}{\omega} \cdot \underset{\sim}{e}) \underset{\sim}{\omega} \times \underset{\sim}{e} \ f\} + \frac{\partial}{\partial \underset{\sim}{c}} \cdot \{\underset{\sim}{\omega} \times \underset{\sim}{e} f\}$$

$$+ \frac{\partial \dot{B} f}{\partial B} + \frac{\partial \dot{\phi} f}{\partial \phi} = G - L. = \bar{J} . \tag{3.2.8}$$

The quantities G and L are some functionals of the distribution function whose formulation is dealt with, in the following sections.

3.3. Collision Geometry and the Interaction Surface:

Consider a collision between molecule 1 described by the coordinates $\underset{\sim}{q}_1$ and molecule 2 whose coordinates are $\underset{\sim}{q}_2$. The location vectors of the two molecules $\underset{\sim}{x}_1$ and $\underset{\sim}{x}_2$ differ negligibly at the instant of collision. For the type of the geometry of the molecule assumed, there exists a common tangent at the point of impact of the two collision partners and also a common normal to the surface of two molecules at this point. Thus a collision between two molecules 1,2 is completely described by the coordinates $(\underset{\sim}{c}_1, \ \underset{\sim}{e}_1, \ \underset{\sim}{\omega}_1, \ B_1, \ \phi_1)$ for molecule 1, $(\underset{\sim}{c}_2, \ \underset{\sim}{e}_2, \ \underset{\sim}{\omega}_2, \ B_2, \ \phi_2)$ for molecule 2 and the common normal $\underset{\sim}{n}$ at the point of impact. An 'interaction surface' enclosing an 'excluded volume' is defined in the case of a binary collision, as the locus traced by the centre of mass of molecule 2, as it moves in contact with molecule 1, fixing the orientation of both the molecules. A point on the interaction surface is separated by a vector $\underset{\sim}{R}$ from

the centre of mass of molecule 1. From the geometry we have (Fig. 3.3.1.)

$$\underset{\sim}{R} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2 \ ; \ d\underset{\sim}{R} = d\underset{\sim}{r}_1 - d\underset{\sim}{r}_2 \tag{3.3.1}$$

so that

$$\underset{\sim}{n} \cdot d\underset{\sim}{R} = \underset{\sim}{n} \cdot d\underset{\sim}{r}_1 - \underset{\sim}{n} \cdot d\underset{\sim}{r}_2 = 0 \tag{3.3.2}$$

Hence $\underset{\sim}{n}$ is also normal to the interaction surface. For the case of a rigid spherocylinder it has already been established by Haight (1965) that an element dS on the interaction surface depends on $\underset{\sim}{e}_1, \underset{\sim}{e}_2, \underset{\sim}{n}$ for a given kind of molecule and is related to an element of surface $d\underset{\sim}{n}$ on a unit sphere by

$$dS = K \ (\underset{\sim}{e}_1, \ \underset{\sim}{e}_2, \ \underset{\sim}{n}) \ d\underset{\sim}{n} \tag{3.3.3}$$

Extending this for the axially elastic sphero-cylinder case. we have

$$dS = K(\underset{\sim}{e}_1, \underset{\sim}{e}_2, \underset{\sim}{n}, \Gamma_1, B_2, \phi_1, \phi_2) \ d\underset{\sim}{n} \tag{3.3.4}$$

where

$$K(\underset{\sim}{e}_1, \underset{\sim}{e}_2, \underset{\sim}{n}, B_1, B_2, \phi_1, \phi_2) = 4a^2 + 2a\{(b_1 + B_1 \cos \phi_1)$$

$$\delta(\underset{\sim}{e}_1 \cdot \underset{\sim}{n})(\underset{\sim}{e}_1 \times \underset{\sim}{n})^2 + (b_2 + B_2 \cos \phi_2) \ \delta(-\underset{\sim}{e}_2 \cdot \underset{\sim}{n}) \ (\underset{\sim}{e}_2 \times \underset{\sim}{n})^2 \}$$

$$+ \{(b_1 + B_1 \cos \phi_1)\delta(\underset{\sim}{e}_1 \cdot \underset{\sim}{n}) + (b_2 + B_2 \cos \phi_2)\delta(-\underset{\sim}{e}_2 \cdot \underset{\sim}{n})\}(\underset{\sim}{e}_1 \times \underset{\sim}{e}_2 \times \underset{\sim}{n})^2 \tag{3.3.5}$$

In Eqn. (3.3.1) $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ are functions of $(\underset{\sim}{e}_1 , \underset{\sim}{n} , B_1, \phi_1)$ and $(\underset{\sim}{e}_2 , \underset{\sim}{n} , B_2, \phi_2)$ respectively, where $\underset{\sim}{e}_1$ and $\underset{\sim}{e}_2$ depend on time of rotating molecules. Thus the interaction surface S is variable with time. In obtaining the collision frequency we need the normal velocity

of a point on the interaction surface. From Eqns. $(2.2.1)$ and $(3.3.1)$ we can write

$$c_{n,s} = \underset{\sim}{n} \cdot \frac{d\underset{\sim}{r}}{dt} = (\underset{\sim}{\omega}_1 \times \underset{\sim}{r}_1 - \underset{\sim}{e}_1 \beta_1 \nu \sin \phi_1) - (\underset{\sim}{\omega}_2 \times \underset{\sim}{r}_2 - \underset{\sim}{e}_2 \beta_2 \nu \sin \phi_2) \qquad (3.3.6)$$

where $c_{n,s}$ is the normal component of the velocity of a point on the interaction surface S.

The interaction surface and the normal velocity of a point on the surface for a collision between an atom and a molecule may be obtained as a special case of the above results by putting

$$b_2 = 0 \ , \ \underset{\sim}{e}_2 = \underset{\sim}{n} \ , \ \underset{\sim}{\omega}_2 = 0 \ , \ \beta_2 = 0 \ \text{and} \ \phi_2 = 0,$$

for the second collision partner viz. atom.

3.4. Collision Frequency :

To write down the Gain and the Loss terms, G and L in Eqn. $(3.2.8)$ we need the number of collisions between type 1 and type 2 molecules taking place during an interval $t, t + dt$ in the region $\underset{\sim}{x} \ , \ \underset{\sim}{x} + d\underset{\sim}{x}$ of the physical space. The assumption of molecular chaos is made in finding an expression for collision frequency. Thus the two sets of molecules considered in the phase space regions $\underset{\sim}{q}_1 \ , \ \underset{\sim}{q}_1 + d\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2 \ , \ \underset{\sim}{q}_2 + d\underset{\sim}{q}_2$ are assumed to be distributed at random without any correlations between linear velocity, position, angular velocity, orientation, maximum amplitude of vibration and the phase angle of vibrations. In other words, all the pre-collision variables of the two sets of molecules, are uncorrelated. For long spherocylinder molecules, chattering collisions, in which the pre-collision variables are strongly

dependent, are possible. The effects of such chattering collisions may be reduced by choosing a small b/a.

A molecule of type 2 has a velocity $(c_2 - c_1)$ relative to the centre of mass of molecule of type 1. Further the normal component of the velocity of a point, on the interaction surface with respect to the centre of mass of molecule 1 is non-zero and is given by Eqn. (3.3.6). Hence the velocity of the centre of mass of molecule 2 in a direction normal to the interaction surface and relative to the surface is given by

$$(c_n)_{2,S} = (c_2 - c_1) \cdot n - c'_{n,c} = (g \cdot n) \qquad (3.4.1)$$

where g is given by Eqn. (2.3.6).

A collision between molecule 2 and molecule 1 (or collision of type 1-2) would take place when the centre of mass of molecule 2 occupies a point on the interaction surface defined. Thus, the molecules of type 2 whose centres of mass are lying inside a cylinder of base area dS on the interaction surface S and length $- (g \, n) \, dt$ normal to the surface (see Fig. 3.3.1) would encounter a molecule of type 1 during a time interval dt. The probable number of type 2 molecules lying inside this cylindrical volume $(- g \cdot n \, dt \, dS)$ in physical space and having co-ordinates between q_2 and $q_2 + d \, q_2$ is

$$f(x, c_2, \omega_2, e_2, E_2, \phi_2; t)(-g \cdot n \, dt \, dS) \, dc_2 \, de_2 \, d\omega_2 \, dB_2 \, d\phi_2$$

This also gives the number of type 1-2 collisions taking place during the time interval dt for one molecule of type 1 present in the phase space q_1, $q_1 + d \, q_1$. Thus the total number of 1-2 collisions taking

place in the phase space q_1 , $q_1 + d\,q_1$ per unit time is given by

$$\{ \int f_1 f_2(-g.n)dS \ dc_2 \ de_2 \ d\omega_2 \ dB_2 \ d\phi_2 \} \ dq_1 \qquad (3.4.2)$$

The number of collisions taking place in a unit volume and unit time known as collision frequency can be written as

$$- \int_{g.n<0} f_1 f_2(g.n)dS \ dc_2 d\omega_2 de_2 \ dB_2 \ d\phi_2 \ dc_1 \ d\omega_1 \ de_1 \ dB_1 \ d\phi_1 \qquad (3.4.3)$$

For the case of collision between an atom and a molecule the collision frequency can be written from Eqn. (3.4.3) as follows: Taking the particle 2 to be an atom, we have $B_2 = 0$, $\phi_2 = 0$, $\omega_2 = 0$ and $e_2 = n$. Further the area dS_1 on the interaction surface S_1, in this case is given by putting $b_2 = 0$ and $e_2 . n = 1$ in Eqns. (3.3.4) and (3.3.5). Thus the frequency of molecule-atom collision is given by

$$- \int_{g_1.n<0} f_1 F_2(g_1.n)dS_1 \ dc_2 \ dc_1 \ de_1 \ d\omega_1 \ dB_1 \ d\phi_1 \qquad (3.4.4)$$

where F_2 is atomic distribution function and

$$g_1 = c_2 - (c_1 + \omega_1 \times r_1 - e_1 B_1 \ v \ sin \ \phi_1) \qquad (3.4.5)$$

3.5. Collision Integral :

A molecule of type 1 loses its identity when it undergoes a collision. Thus the number of molecules of type 1 lost from the phase volume q_1 , $q_1 + dq_1$ during a time interval dt due to collisions is given by

$$\{ \int f_1 f_2 \gamma(-g.n) \ dS \ dc_2 \ d\omega_2 \ de_2 \ dB_2 \ d\phi_2 \} \ dq_1 \ dt. \qquad (3.5.1)$$

where $\quad \gamma(y) = 0 \quad$ for $y < 0$ $\qquad\qquad$ (3.5.2)
$\qquad\qquad\qquad = y \quad$ for $y > 0$

The quantity inside the bracket corresponds to the loss term L in the Eqn. (3.2.8). By choosing properly the pre-collision variables (x , c_1', e_1 ,ω_1' , B_1' , ζ_1') and (x , c_2' , e_2 ,ω_2' ,B_2' ,ϕ_2') for the two sets of molecules, it is possible to obtain molecules with post collision variables as (x , c_1, ω_1, e_1, B_1, ϕ_1) and (x , c_2, ω_2, e_2, B_2, ϕ_2). In such a collision a molecule of type 1 is generated. Using the expression for the collision frequency Eqn. (3.4.3), we can write down the total number of 1'- 2' collisions occurring in time dt as

$$\{ \int f_1' c_2' \gamma(-g' \cdot n) dS \; dc_2' \; d\omega_2' \; de_2 \quad dB_2' \; d\phi_2' \} \; dc_1' \; dt \qquad (3.5.3)$$

From Liouville's theorem of statistical mechanics we have for the conservation of phase volume.

$$dc_1' dc_2' \; d\omega_1' \; d\omega_2' \; dB_1' \; dB_2' \; d\phi_1' \; d\phi_2' =$$

$$\qquad\qquad\qquad\qquad (3.5.4)$$

$$dc_1 \; dc_2 \; d\omega_1 \; d\omega_2 \; dB_1 \; dB_2 \; d\phi_1 \; d\phi_2$$

It can also be shown that

$$(g \cdot n) = -(g' \cdot n) \qquad\qquad (3.5.5)$$

Using these results, the number of 1'- 2' collisions may be written as

$$\{ \int f_1' f_2' \; \gamma(-g \cdot n) dS \; dc_2 \; d\omega_2 \; de_2 \; dB_2 \; d\phi_2 \} \; dc_1 \; dt \qquad (3.5.6)$$

This also gives the number of molecules of type 1, generated in time dt, in space q_1, $q_1 + d \; q_1$. Hence the quantity in the brackets in

Eqn.(3.5.6) corresponds to the gain term G in Eqn. (3.1.7). Thus
we have the expression for the gain and loss terms for molecules of
type 1, lying in q_1, $q_1 + dq_1$. From this we can write the collision
integral $\bar{J}$ for the molecules in q , $q + dq$ by dropping the
subscript 1 and changing subscript 2 to 1 as

$$\bar{J} = \int f' \, f_1' \, \gamma(g.n) \, dS \, d\tau_1 + \int f f_1 \, \gamma(-g.n) d\xi \, d\tau_1 \qquad (3.5.7)$$

where

$$d\tau_1 = dc_1 \, d\omega_1 \, de_1 \, dB_1 \, d\phi_1 \qquad (3.5.8)$$

This completes the formulation of the Boltzmann equation for a gas
with axially elastic sphero-cylinder molecules.

3.6. <u>Moment Equations</u> :

The corresponding Maxwell transfer equation for this case may
be obtained as usual by multiplying both sides of the Boltzmann
equation (3.2.8) by a molecular property $\psi(x , c , e , \omega , B, \phi)$
and integrating with respect to c , ω, e , B and ϕ . This
gives us the following equation

$$\int \left[\frac{\partial f}{\partial t} + c \cdot \frac{\partial f}{\partial x} + F \cdot \frac{\partial f}{\partial c} + \frac{\partial}{\partial \omega} \cdot \left\{ \frac{J_1 - J_2}{J_1} (\omega.e) \, (\omega \times c) f \right\} \right.$$

$$\left. + \frac{\partial}{\partial e} \cdot (\omega \times e) f + \frac{\partial \dot{B} f}{\partial B} + \frac{\partial \dot{\phi} f}{\partial \phi} \right] \psi(x,c,e,\omega,B,\phi) \, d\tau$$

$$= \int \bar{J} \, \psi \, d\tau \qquad (3.6.1)$$

Using the following notation for the moment of f

$$\int \psi(\underset{\sim}{x},\underset{\sim}{c},\underset{\sim}{\omega},\underset{\sim}{e},B,\phi,t) f \, d\underset{\sim}{c} \, d\underset{\sim}{\omega} \, d\underset{\sim}{e} \, dB \, d\phi = n(\underset{\sim}{x},t) \, \tilde{\psi}(\underset{\sim}{x},t) \tag{3.6.2}$$

where $n(\underset{\sim}{x},t)$ is the number density of molecules at a point $\underset{\sim}{x}$ and time t, the Maxwell transfer equation, for the case where ψ is a function of only $\underset{\sim}{c}$, $\underset{\sim}{\omega}$ and B may be simplified to the form

$$\frac{\partial n \, \overline{\psi}}{\partial t} + \frac{\partial . n \overline{c \, \psi}}{\partial x} - n \{ \underset{\sim}{F} \cdot \overline{\frac{\partial \psi}{\partial \underset{\sim}{c}}} + \frac{J_1 - J_2}{J_1} \overline{(\underset{\sim}{\omega}_1 \cdot \underset{\sim}{e}_1) \, \underset{\sim}{\omega} \times \underset{\sim}{c}}.$$

$$\overline{\frac{\partial \psi}{\partial \underset{\sim}{\omega}}} + \dot{B} \overline{\frac{\partial \psi}{\partial \cdots}} \} = \int \psi(f'f_1' - ff_1) \, \gamma(-\underset{\sim}{g} \cdot \underset{\sim}{n}) \, K(\underset{\sim}{c}, \underset{\sim}{e}_1, \underset{\sim}{n},$$

$$B, B_1, \phi, \phi_1) \, d\underset{\sim}{n} \, d\underset{\sim}{c}_1 \, d\underset{\sim}{\omega}_1 \, d\underset{\sim}{e}_1 \, dB_1 \, d\phi_1 \tag{3.6.3}$$

in which Eqn. (3.3.4) is used for dS. The right hand side of this equation, which is the change $(\Delta \psi)_{col}$ in the property ψ due to collisions, may be written in different forms by effecting some changes in the variables of integration as done by Haight (1965). Thus one of the useful forms is

$$(\Delta \psi)_{col} = \frac{1}{2} \int (\psi_1' + \psi' - \psi_1 - \psi) \, ff_1 \, \gamma(-\underset{\sim}{g} \cdot \underset{\sim}{n}) K \, d\underset{\sim}{n} \, d\tau_1 \tag{3.6.4}$$

The primed quantities $(\underset{\sim}{c}_1', \underset{\sim}{\omega}_1', B_1', \phi_1')$ and $(\underset{\sim}{c}', \underset{\sim}{\omega}', B', \phi')$ are the pre-collision collision variables of two colliding molecules giving rise to molecules with post collision variables $(\underset{\sim}{c}_1, \underset{\sim}{\omega}_1, B_1, \phi_1)$ and $(\underset{\sim}{c}, \underset{\sim}{\omega}, B, \phi)$. In the present case, a summational invariant ψ is defined, which satisfies the condition

$$\psi_1' + \psi' - \psi_1 - \psi = 0 \tag{3.6.5}$$

Thus, in the Maxwell transfer equation, if ψ is a summational

invariant, the collision integral on the right hand side, vanishes. A careful examination of the collision dynamics, enables us to find the following summational invariants

$$
\psi = \begin{cases} 1 \\ n \, \underset{\sim}{c} \\ \frac{1}{2} m \, \underset{\sim}{c}^2 + \frac{1}{2} J_1 \, \omega_\perp^2 + \frac{1}{2} s(2\eta)^2 \\ \text{any function of } \underset{\sim}{e} \\ \text{any function of } \omega_{||} \\ \text{any function of } \phi \end{cases}
\tag{3.6.6}
$$

By choosing the first three of these, the familiar conservation equations for mass, linear momentum and energy may be written as follows:

$$
\frac{\partial n}{\partial t} + \frac{\partial}{\partial \underset{\sim}{x}} \cdot n\underset{\sim}{u} = 0
$$

$$
\rho \left(\frac{\partial \underset{\sim}{u}}{\partial t} + \underset{\sim}{u} \, \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{x}} \right) = \frac{\partial}{\partial \underset{\sim}{x}} \cdot \underset{\sim}{p} + \rho \, \underset{\sim}{F}
\tag{3.6.7}
$$

$$
\frac{7}{2} kn \left(\frac{\partial T}{\partial t} + \underset{\sim}{u} \cdot \frac{\partial T}{\partial \underset{\sim}{x}} \right) = - \frac{\partial \cdot \overline{\underset{\sim}{q}}}{\partial \underset{\sim}{x}} + \underset{\sim}{p} : \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{x}}
$$

where $\underset{\sim}{u}$, T, $\overline{\underset{\sim}{q}}$ and $\underset{\sim}{p}$ are defined as the following moments of the distribution function f :

$$
\underset{\sim}{u} = \frac{1}{n} \int \underset{\sim}{c} \, f \, d\tau
$$

$$
T = \frac{1}{\frac{7}{2} nk} \int \left\{ \frac{1}{2} m \, \underset{\sim}{c}^2 + \frac{1}{2} J_1 \, \omega_\perp^2 + \frac{1}{2} s(2\eta)^2 \right\} f \, d\tau
\tag{3.6.8}
$$

and
$$
\underset{\sim}{p} = \int m \, \underset{\sim}{c} \, \underset{\sim}{c} \, f \, d\tau
$$

$$
\overline{\underset{\sim}{q}} = \int \underset{\sim}{c} \left\{ \frac{1}{2} m \, \underset{\sim}{c}^2 + \frac{1}{2} J_1 \, \omega_\perp^2 + \frac{1}{2} s(2\eta)^2 \right\} f \, d\tau
$$

Out of these moments, u and T refer, respectively, to the macroscopic velocity and temperature; p and $\bar{q}$ are related to the pressure tensor P and the heat flux vector Q by the following relationships:

$$\bar{q} = Q + \rho \frac{u^2}{2} u \qquad (3.6.9)$$

and

$$p = P + \rho \, u \, u$$

It should be noted that, though the angular momentum is conserved during a collision, it is not a summational invariant due to the two distinct location vectors chosen for the two collisional partners.

3.7. H-Theorem and the Equilibrium Distribution :

In this section, an equilibrium solution is obtained for the Boltzmann Equation $(3.2.8)$, through an H-Theorem. The number of molecules with dynamic variables q_1 in a phase volume q_1, $q_1 + dq_1$ is given by $f(q_1, t) \, dq_1$. If the state of a gas changes in a time interval dt, this number also changes to $(f_1 + \Delta f_1) \, dq_1$. The fractional change in the number of molecules accompanying a change of the state of the gas is $(\Delta f_1/f_1) \, dq_1$ or $(\Delta \ln f_1) \, dq_1$. Such a change takes place for molecules with different dynamic variables. Thus, it is seen that $\ln f$ is an important molecular property associated with the state of a gas. Choosing $\psi = \ln f$ in the Maxwell transfer Equation $(3.6.3)$, we get

$$\frac{\partial n \, \overline{\ln f}}{\partial t} + \frac{\partial}{\partial x} \cdot (n\underline{c} \, \overline{\ln f}) = \frac{1}{2} \int \ln\left(\frac{ff_1}{f'f_1'}\right) ff_1 \, \gamma(-g \cdot n) K \, dn \, d\tau_1 \, d\tau \qquad (3.7.1)$$

Further, it can be shown that for the case of an axially elastic spherocylinder particle the right hand side of Eqn. (3.7.1) is always negative or at most equal to zero. In the case of rigid spherocylinder molecules a similar result was used by Haight (1965). Thus for a uniform case, we can write the above equation as

$$\frac{dH}{dt} = \frac{1}{2} \int \ln \left(\frac{ff_1}{f'f_1'}\right) ff_1 \; \gamma(-g \cdot n) \; K \; dn \; d\tau \; d\tau_1 \qquad (3.7.2)$$
$$\leq 0$$

where

$$H = n \; \overline{\ln f} = \int f \ln f \; d\tau \qquad (3.7.3)$$

Eqn. (3.7.2) is the statement of the H-Theorem. Following the arguement given by Chapman and Cowling (1970), it can be concluded that H decreases monotonically to a constant value corresponding to the case $\frac{dH}{dt} = 0$. Further, it is also known that this corresponds to maximum entropy or statistical equilibrium. Thus for equilibrium, we have from Eqn. (3.7.2)

$$\ln f_1' + \ln f' = \ln f_1 + \ln f \qquad (3.7.4)$$

Comparing this with Eqn. (3.6.5) it can easily be seen that $\ln f$ is a summational invariant or a linear combination of the summational invariants (3.6.6). Thus we can write $\ln f$ in the form

$$\ln f = \alpha_1 + \alpha_2 \cdot c + \alpha_3 \{\frac{1}{2}mc^2 + \frac{1}{2}J_1\omega_1^2 + \frac{1}{2} s(2B)^2\} + \alpha_4 F_1(\omega_{11}) + \alpha_5 \; G_1(\phi) \qquad (3.7.5)$$

where α_1, α_2, α_3, α_4 and α_5 are the quantities which may be related to physical parameters like number density, temperature and velocity of the gas. Using the normalisation relationship

(3.6.2) and the definitions (3.6.8) of velocity and temperature the Eqn. (3.7.5) can be written in a standard form as

$$f = \frac{n}{4\pi}\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{J_1}{2\pi kT}\right)\left(\frac{8s}{\pi kT}\right)^{1/2}\exp\left\{-\frac{mc^2+J_1\omega_1^2+s(2E)^2}{2kT}\right\} F(\omega_{11})G(\phi) \quad (3.7.6)$$

where

$$\int_{-\infty}^{\infty} F(\omega_{11})\ d\omega_{11} = 1 \quad (3.7.7)$$

and $G(\phi)$ is the distribution function for the phase angle ϕ, of the vibrational state of the molecules. In the absence of any other information, the distribution $G(\phi)$ for ϕ will be assumed to be uniform. Thus we shall take

$$G(\phi) = \frac{1}{2\pi} \quad (3.7.8)$$

Further in writing Eqn. (3.7.5) the following approximation is employed:

$$\text{erf}\left(\sqrt{\frac{2s}{kT}}\,B_{max}\right) = \text{erf}\sqrt{\frac{T_D}{T}} \simeq \frac{\sqrt{\pi}}{2} \quad (3.7.9)$$

This is justifiable as the value of T_D for N_2 is $113000°K$ (see Table 2.1.1). Thus we have the Maxwellian distribution for the case of a vibrationally relaxing diatomic gas. In the next chapter two solutions for the plane shock structure problem is discussed for a vibrationally relaxing diatomic gas.

FORMULATION OF SHOCK STRUCTURE PROBLEM

4.1. Introduction :

Due to the complexity of the collision terms in the Boltzmann equation (especially the gain term) it has not been possible (till now) to solve the equation even for problems with simple boundary conditions To overcome this difficulty some models for the Boltzmann equation were proposed by making some reasonable assumptions about the collision proc by Bhatnagar, Gross and Krook (1954), Gross and Jackson (1959) for the monatomic gas case and Brau (1969), Morse (1964), Hanson and Morse (196' for the diatomic gas case. For the case of monatomic gases, the model equation was solved numerically by using an iteration scheme by Liepmann et al (1962).

Another approach to solve a gasdynamic problem from a molecular point of view, consists in choosing a suitable ansatz for the unknown distribution function leaving a few free parameters in it. These free parameters are determined by using as many moments of the Boltzmann equation as the number of free parameters in the ansatz. The solution thus obtained is only an approximate one and depends strongly on the fo: of the ansatz used and the choice of the molecular properties used in the moment equations.

4.2 Ansatz for the Distribution Function :

Mott-Smith (1951) proposed a bimodal ansatz for the distribution function inside a plane shock wave in a monatomic gas considering the

physics of the problem. Following the two step analysis for shock

waves in a diatomic gas given by Talbot and Scala (1961) within the

frame work of Navier-Stokes theory, Haight (1965) extended the Mott-

Smith bimodal theory to a diatomic case. He proposed a trimodal

distribution function for the shock problem. Both Mott-Smith and

Haight used moment methods to solve for the unknown or the free

parameters in the ansatz. The ansatz proposed by Haight is capable of

predicting only the effects of rotational excitation on the structure

of a shock wave. In the present analysis vibrational effects are also

included in the formulation. Further in Chapter 5 the dissociation

effects are also considered for the shock structure problem.

A more general ansatz was proposed by Weitzsch (1961) for the

distribution function in the case of strong departure from thermodynami

equilibrium as an integral superposition of Maxwellians with suitable

weighting functions. The integral representation may be replaced by a

quadrature formula as given by Narasimha and Deshpande (1968) for the

distribution function as

$$f = \sum_{\alpha=1}^{N} w_\alpha F_\alpha \qquad (4.2.1)$$

where F_α is a Maxwellian built up using (u_α, T_α, n_α) and w_α is the

product of the weighting function chosen in the integral representation

and the weights in the appropriate quadrature formula. It can easily

be shown that the Mott-Smith bimodal ansatz is a particular case of the

general form (4.2.1). Extending a similar representation to the

diatomic case, we have Haights' trimodal ansatz as a particular case of

Eqn. (4.2.1). The choice of the parameters used in building up the

Maxwellians is arbitrary in the general form of the distribution.
However, if the choice is made on the basis of the physics of the
problem at hand, one can expect a better representation of f.
Further the representation of f may be improved by choosing as large
an N as possible for a given problem. The value of the number N is
limited by the magnitude of computational work involved and the ability
to guess the parameters, to build up the Maxwellians, for a given
physical situation.

4.3 Quadrimodal Hypothesis :

Scala and Talbot (1963) obtained the structure of a shock wave
in a vibrationally and rotationally relaxing diatomic gas from a
continuum approach. **For this they** extended their earlier analysis
(1961) by defining a third temperature for the vibrational degrees
of freedom. However for the present analysis the experimentally
established fact $\tau_v \gg \tau_r > \tau_t$ is used to visualise a three step
shock. In the initial narrow region (translational shock) only the
translational degrees of freedom are assumed to be excited fully and
in the central zone (rotational shock) the rotational degrees of freedom
are expected to attain equilibrium. In both of these regions the
vibrational excitation is taken to be negligible. Finally, in the
broad tail of the shock (vibrational shock) the vibrational excitations
occur completely. With such a picture for a shock wave, it is possible
to choose four sets of parameters to build up four Maxwellians. (In
an actual shock these three distinct regions do not exist). These
Maxwellians are used in (4.2.1) to arrive at a quadrimodal distribution
function for the shock problem.

The four Maxwellians $f_i, i = 1,4$, thus chosen correspond to the following four states of the gas:

1. uniform free stream equilibrium condition.

2. intermediate state existing at the end of the translational shock.

3. intermediate state existing at the end of the rotational shock.

4. uniform down stream equilibrium conditions.

The parameters used in building up these four Maxwellians are obtained in the next section.

4.4. <u>Parameters in the Maxwellians</u> :

Maxwellian f_1 - For a given upstream Mach number M_1, temperature T_1 and pressure p_1, the parameters for the Maxwellian f_1 may be written down easily. As the rotational degrees of freedom are excited completely, at the upstream temperatures considered (T_1= 293°, 400°,500° K), the value of rotational temperature (T_{r_1}) for the upstream gas is the same as that of the translational temperature. However, the vibrational excitations of molecules at such low (upstream) temperatures are neglegible and hence the vibrational temperature T_{v_1}, may be taken to be zero.

Thus we have

$$T_{t_1} = T_{r_1} = T_1 \; ; \quad T_{v_1} = 0 \qquad\qquad (4.4.1)$$

As a consequence of zero vibrational temperature, the distribution function corresponding to vibrational degrees of freedom, in the Maxwellian f_1 (See Eqn. 3.7.6) becomes a Dirac delta function

i.e. $\lim\limits_{T_{v_1} \to 0} [\{\frac{8s}{\pi k T_{v_1}}\}^{1/2} \exp(-\frac{s(2B)^2}{2k T_{v_1}})] = \delta(B)$ (4.4.2)

Further in absence of vibrational excitation, the distribution

$G(\phi)$ for the phase angle ϕ is also dropped. Thus we can write

f_1, finally as

$$f_1 = \frac{n_1}{4\pi}(\frac{m}{2\pi kT_1})^{3/2}(\frac{J_1}{2\pi kT_1})\exp\{-\frac{m(c - i\,u_1)^2 + J_1\omega_1^2}{2kT_1}\}\,\delta(B)\,F(\omega_{1j})\ (4.4.3)$$

Maxwellian f_2 - The translational temperature (T_{t_2}), the velocity

(u_2) and the number density (n_2) of the gas at the end of the first

zone may be fixed by using the Rankine-Hugoniot condition for

monatonic case $(\gamma = 5/3)$. However, the rotational and vibrational

temperatures $(T_{r_2},\ T_{v_2})$ of the gas are frozen at values corresponding

to their free stream values.

i.e.
$$\frac{T_2}{T_1} = \frac{21}{80}\,(1 + \frac{25/7}{M_1^2})\,(M_1^2 - \frac{5}{21})$$

$$\frac{n_1}{n_2} = \frac{u_2}{u_1} = \frac{1}{4}\,(1 + \frac{25/7}{M_1^2})$$ (4.4.4)

$$T_{t_2} = T_2\ ;\ T_{r_2} = T_1\ ;\ T_{v_2} = T_{v_1} = 0$$

where

$$M_1^2 = u_1^2/(7/5\,\frac{k}{m}\,T_1)$$ (4.4.5)

Thus we have the Maxwellian f_2 as

$$f_2 = \frac{n_2}{4\pi}(\frac{m}{2\pi kT_2})^{3/2}(\frac{J_1}{2\pi kT_1})\exp\{-\frac{m(c - i\,u_2)^2}{2k\,T_2} - \frac{J_1\omega_1^2}{2kT_1}\}\,\delta(B)\,F(\omega_{1j})\quad (4.4.6)$$

Maxwellian f_3 - Further the translational and rotational temperatures (T_{t_3}, T_{r_3}), the number density (n_3) and the velocity (u_3) of the gas at the end of the rotational shock may be fixed using the Rankine-Hugoniot conditions for a rotationally relaxing diatomic gas $(\gamma = 7/5)$, while the vibrational temperature continues to remain at its upstream value (zero).

ie
$$\frac{T_3}{T_1} = \frac{7}{36} (1 + \frac{5}{M_1^2}) (M_1^2 - \frac{1}{7})$$

$$\frac{n_1}{n_3} = \frac{u_3}{u_1} = \frac{1}{6} (1 + \frac{5}{M_1^2}) \qquad (4.4.7)$$

$$T_{t_3} = T_{r_3} = T_3 \; ; \; T_{v_3} = 0.$$

Knowing these quantities the Maxwellian f_3 may be written as

$$f_3 = \frac{n_3}{4\pi} (\frac{m}{2\pi k T_3})^{3/2} (\frac{J_1}{2\pi k T_3}) \exp \{\frac{m(\underline{c} - \underline{i} \, u_3)^2 + J_1 \, \omega_\perp^2}{2k \, T_3}\} \delta(B) \mathbb{F}(\omega_{11}) \qquad (4.4.8)$$

Maxwellian f_4 - The uniform downstream condition of the gas may be determined by using the three familliar conservation equations

$$n_1 u_1 = n_4 u_4$$

$$r_1 (u_1^2 + \frac{k}{m} T_1) = n_4 (u_4^2 + \frac{k T_4}{m}) \qquad (4.4.9)$$

$$u_1^2 + 7 \frac{k}{m} T_1 = u_4^2 + 9 \frac{k}{m} T_4$$

The values of n_4, u_4, T_4 predicted by these equations are exact for perfect gases. However in the present work the more realistic values for n_4, u_4 and T_4 for nitrogen, considering real gas effects, calculated by Athye and Peng (1962) are used. Recently Law and Bristov (1969) have given more exact values for the downstream parameters for normal shocks in a tabular form, for both nitrogen and oxygen. Thus we have

$$f_4 = \frac{n_4}{8\pi^2}\left(\frac{m}{2\pi kT_4}\right)^{3/2}\left(\frac{J_1}{2\pi kT_4}\right)\left(\frac{8s}{\pi kT_4}\right)^{1/2}\exp\left\{-\frac{m(\underline{c}-\underline{i}u_4)^2+J_1\omega_1^2+s(2B)^2}{2kT_4}\right\}F(\omega_{11}) \quad (4.4.10)$$

in which all the three temperatures T_{t_4}, T_{r_4} and T_{v_4} have the same value.

Finally we have the ansatz (4.2.1) in the form

$$f = w_1 f_1 + w_2 f_2 + w_3 f_3 + w_4 f_4 \quad (4.4.11)$$

where w_i, $i = 1,4$ are the unknown functions of the distance x varying through the shock. The boundary conditions on these functions may be written as

$$w_1 = 1; \quad w_2 = w_3 = w_4 = 0 \quad \text{for} \quad x \to -\infty$$

$$(4.4.12)$$

$$w_1 = w_2 = w_3 = 0; \quad w_4 = 1 \quad \text{for} \quad x \to +\infty$$

Thus the molecules in the shock belong to one of the four states described by the four Maxwellians $f_i, i = 1,4$.

4.5   Macroscopic Quantities :

The gas dynamic variables like density, velocity and various temperatures, inside the shock may be written in terms of the weight functions w_i, $i = 1,4$ and the parameters in the four Maxwellians used. By using the definitions for the macroscopic quantities in Eqns. (3.2.2.) and (3.6.8.) and the expression for f given by Eqn. (4.4.12) we can write down the following expressions:

.

$$\frac{n}{n_1} = (w_1 + \frac{n_2}{n_1} \, w_2 + \frac{n_3}{n_1} \, w_3 + \frac{n_4}{n_1} \, w_4 \,)$$

$$\frac{u}{u_1} = \frac{n_1}{n}$$

$$\frac{T_t}{T_1} = \{w_1 + \frac{n_2}{n_1} \frac{T_2}{T_1} \, w_2 + \frac{n_3}{n_1} \frac{T_3}{T_1} w_3 + \frac{n_4}{n_1} \frac{T_4}{T_1} \, w_4$$

$$+ \frac{7}{15} \, M_1^2 \, (-\frac{u}{u_1} + w_1 + w_2 \, \frac{u_2}{u_1} + w_3 \frac{u_3}{u_1}$$

$$+ w_4 \frac{u_4}{u_1} \,)\} \, / \, (n/n_1) \tag{4.5.1}$$

$$\frac{T_r}{T_1} = \{w_1 + \frac{n_2}{n_1} w_2 + \frac{n_3}{n_1} \frac{T_3}{T_1} \, w_3 + \frac{n_4}{n_1} \frac{T_4}{T_1} \, w_4 \}/(\frac{n}{n_1})$$

$$\frac{T_v}{T_1} = \{ \frac{n_4}{n_1} \frac{T_4}{T_1} \, w_4\} \, / \, (n/n_1)$$

Thus, once we know the variation of the weight functions with x we can calculate the various quantities, using these equations, to obtain the shock profiles.

4.6 Moment Equations :

As indicated earlier, after choosing a form for the distribution function for the problem, the unknown parameters (weight functions) are determined by satisfying appropriate number of moments of the Boltzmann equation. The molecular property chosen for the moment equation should, of course, be relevant to the problem concerned.

From the continuity equation (4.1.4), we get a simple algebraic equation for w_i, $i = 1,4$ as

$$w_1 + w_2 + w_3 + w_4 = 1 \tag{4.6.1}$$

The other two conservation equations (momentum and energy)along with the quadrimodal ansatz, Eqn. (4.4.12), do not yield any additional independent equations for w_i's. Thus we need three more suitable moment equations to complete the system of equations for w_i's. For the relaxation flow situation, two of the relevant molecular properties chosen are the rotational energy and vibrational energy. The third choice closely follows the bimodal theory and for simplicity the c_x^2 moment is used.

From Eqns. (3.5.3) and (3.5.4), we can write down the steady one dimensional Maxwell transfer equation as

$$\frac{d}{dx} \int c_x \psi f d\tau = -\frac{1}{2} \int (\psi_1' + \psi' - \psi_1 - \psi) \gamma(-\underset{\sim}{g} . \underset{\sim}{n}) . f f_1 K d\underset{\sim}{n} d\tau_1 d\tau \qquad (4.6.2)$$

Substituting for f from Eqn. (4.4.9) in this equation we get

$$\sum_{i=1}^{4} \frac{dw_i}{dx} \int c_x \psi f_i d\tau = \frac{1}{2} \sum_{i,j=1}^{4} w_i w_j I_{ij}(\psi) \qquad (4.6.3)$$

where $I_{ij}(\psi)$ is the collision integral given by

$$I_{ij}(\psi) = \int (\psi_1' + \psi' - \psi_1 - \psi) \gamma(-\underset{\sim}{g} . \underset{\sim}{n}) f_i f_{ij} K d\underset{\sim}{n} d\tau_1 d\tau \qquad (4.6.4)$$

having the symmetry property

$$I_{ij}(\psi) = I_{ji}(\psi) \qquad (4.6.5)$$

Putting $\psi = c_x^2$ we get from (4.6.3)

$$\sum_{i=1}^{4} n u(u_i^2 + \frac{3k}{m} T_{t_i}) \frac{dw_i}{dx} = \frac{1}{2} \sum_{i,j=1}^{4} w_i w_j I_{ij}(c_x^2) \qquad (4.6.6)$$

Similarly for $\psi = \frac{1}{2} J_1 \omega_\perp^2$, we get

$$(4.6.7)$$

$$\sum_{i=1}^{4} nu(k \, T_{r_i}) \frac{dw_i}{dx} = \frac{1}{2} \sum_{i,j=1}^{4} w_i \, w_j \, I_{ij} \left(\frac{1}{2} J_1 \omega_\perp^2\right)$$

and for $\psi = s \, (2B)^2/2$, we have

$$(4.6.8)$$

$$\sum_{i=1}^{4} nu(k \, T_{v_i}) \frac{dw_i}{dx} = \sum_{i,j=1}^{4} w_i \, w_j \, I_{ij} \left(\frac{1}{2} s(2B)^2\right)$$

The distance x is non-dimensionalised by using the mean free path λ_1 of the upstream gas (equivalent rigid sphere molecule). Further the quantities in the left hand side of the above equations may be written as functions of M_1, the upstream Mach number. The above three equations can thus be rewritten as

$$(4.6.9)$$

$$\sum_{i=1}^{4} C_{ki} \frac{dw_i}{d\xi} = \frac{1}{2} \sum_{i,j=1}^{4} w_i \, w_j \, I_{kij} \qquad k = 1,3$$

where coefficients C_{ki} are given as the functions of the free stream Mach number M_1 and the various ratios defined earlier (see section 4.4) as follows:

$$C_{1i} = \left(\frac{u_i}{u_1}\right)^2 + \left(\frac{15}{7 \, M_1^2}\right) \left(\frac{T_{t_i}}{T_1}\right)$$

$$(4.6.10)$$

$$C_{2i} = \left(\frac{5}{7 \, M_1^2}\right) \left(\frac{T_{ri}}{T_1}\right)$$

$$C_{3i} = \left(\frac{5}{7 \, M_1^2}\right) \left(\frac{T_{v_i}}{T_1}\right)$$

and the collision coefficients I_{kij} are given by

$$I_{1ij} = \frac{1}{nu\ u_1^2\ \lambda_1}\ I_{ij}(o_x^2)$$

$$I_{2ij} = \frac{1}{mn\ uu_1^2\lambda_1}\ I_{ij}(\tfrac{1}{2}\,J_1\,\omega_\perp^2) \tag{4.6.11}$$

$$I_{3ij} = \frac{1}{mn\ uu_1^2\lambda_1}\ I_{ij}\ (\tfrac{1}{2}\,s(2B)^2)$$

The collision integrals appearing on the right hand side of the Eqns. (4.6.9) are 22 fold integrals. The evaluation of these has been shown in Appendix A. Out of the 22 fold integrals only 16 fold integrations could be performed analytically for most of the cases. The remaining 6 fold integrations have been carried out numerically using the Monte Carlo technique, the details of which are given in Chapter 6. The set of equations (4.6.1) and (4.6.9) have been solved numerically and shock profiles have been calculated for four Mach numbers $(M_1 = 15, 20, 25, 30)$ and three upstream pressures. $(p_1 = 0.1, 0.01, 0.001$ atmosphere). The results obtained are discussed in Chapter 7.

4.7 Trimodal Hypothesis for the Shock :

As the relaxation time for the translational and rotational degrees of freedom are nearly of the same order $(\tau_t \sim \tau_r)$ it is possible to further simplify the quadrimodal formulation by a merger of the translational and rotational relaxation zones. This reduces the number of Maxwellians used in distribution function by one and hence we have a trimodal distribution function. The molecules inside the shock belong either to the upstream equilibrium state, f_1, the downstream Maxwellian state, f_4, or an intermediate equilibrium state with no vibrational excitations, f_3. The distribution function in this case is given by

$$f = w_1 f_1 + w_3 f_3 + w_4 f_4 \qquad (4.7.1)$$

where w_1, w_3 and w_4 are the three unknown weight functions to be determined.

As in the earlier case, a moment method is used to determine the weight functions. For the present case, in addition to one algebraic equation provided by the three conservation equations given by Eqn. (4.6.1) two additional moment equations, viz., vibrational energy and rotational energy, are used. Thus the three equations for the present formulation are given by Eqns. (4.6.1) and (4.6.9) $(k = 2,3)$ with $w_2 = 0$ in them. The boundary conditions given by Eqn. (4.4.12) hold good for the weight functions w_1, w_3 and w_4. Solving these equations, the shock profiles have been obtained for 6 Mach numbers $(M_1 = 12,15,18,20,25,30)$ and three upstream pressure $(p_1 = 0.1, 0.01, 0.001$ atmosphere). A discussion of these results is given in Chapter 7.

The next chapter gives a formulation for the shock structure problem considering the dissociation effects.

SHOCK STRUCTURE WITH DISSOCIATION EFFECTS

5.1. Introduction :

We have, so far considered the shock wave structure in a diatomic
gas with only the vibrational degrees excited to a limited extent so
that no molecular dissociation takes place.   This postulate is valid a
only moderately high Mach numbers.   As the Mach number increases the
degree of dissociation in the diatomic gas behind the shock wave become:
increasingly larger.   Thus, when $M_1 = 20$, $T_1 = 300^\circ K$, $p_1 = 5$ mm Hg.,
the degree of dissociation in the case of nitrogen is approximately 35%
(Fig. (5.1.1) gives the degree of dissociation behind a normal shock in
nitrogen for various upstream Mach numbers and pressures). It is,
therefore, necessary to include the effects of dissociation in the
analysis of the shock structure at these high Mach numbers.

The analysis outlined in the Chapters 2, 3, 4 has to be modified
in two ways.   Firstly, because of the appearance of a second species,
the atom, due to the onset of molecular dissociation, an additional
Boltzmann equation has to be introduced governing the distribution func
of the atom species.   Secondly, additional collision terms appear on
the right hand side of the Boltzmann equation for the diatomic species
representing dissociative and recombinative collisions corresponding to
atom - molecule collisions.   Thus, the problem reduces to the calculati
of the shock structure in a chemically reacting mixture of two species,
atoms and molecules.   The corresponding two Boltzmann equations may be
written formally as:

$$\frac{Df}{Dt} = [f,f] + [f,F] - [f,f]_{dis} - [f,F]_{dis} + [F,F,f]_{recomb} + [F,F,F]_{recomb}$$

$$(5.1.1)$$

$$\frac{DF}{Dt} = \{F,F\} + \{f,F\} + \{f,f\}_{dis} + \{f,F\}_{dis} - \{F,F,f\}_{recomb} - \{F,F,F\}_{recomb} \quad (5.1.2)$$

where f and F are the distribution functions for the molecules

and atoms respectively. The various collision terms on the right

hand sides of equations (5.1.1) and (5.1.2) are defined as follows:

i) $[f,f]$: is the net gain in number of molecules per unit time due

              to 'non-reacting' collisions between two molecules

              as already obtained in Eqn. (3.4.3) as $\bar{J}$.

ii) $\{f,F\}$: is the net gain in number of molecules per unit volume

              per unit time due to 'non-reacting' collisions

              between a molecule and an atom. This term can be

              obtained as a special case of (i) above.

iii) $[f,f]_{dis}$ is the number of molecules lost per unit volume

              per unit time due to dissociative collisions

              between two molecules.

iv) $[f,F]_{dis}$: is the number of molecules lost per unit volume

              per unit time due to dissociative collisions

              between a molecule and an atom.

v) $[F,F,f]_{recomb}$ is the number of molecules gained per unit volume

              per unit time due to (three body) collisions

              between two atoms in presence of a molecule

              resulting in recombination.

vi) $[F,F,\dot{F}]_{recomb}$: is the number of molecules gained per unit volume per unit time due to (three body) collisions between two atoms in presence of a third atom resulting in recombination.

vii) $\{F,F\}$: is the net gain in number of atom per unit volume per unit time due to elastic collisions between two atoms. This can also be written as a special case of (i) above or even directly.

viii) $\{f,F\}$: is the net gain in number of atoms per unit volume per unit time due to 'non reacting' collisions between a molecule and an atom. This can be obtained as a special case of (i).

ix) $\{f,f\}_{dis}$: is the number of atoms gained per unit volume per unit time due to dissociative collisions between two molecules.

x) $\{f,F\}_{dis}$: is the number of atoms gained per unit volume per unit time due to dissociative collisions between a molecule and an atom.

xi) $\{F,F,f\}_{recomb}$: is the number of atoms lost per unit volume per unit time due to (three body) collisions between two atoms in presence of a molecule

xii) $\{F,F,F\}_{recomb}$: is the number of atoms lost per unit volume per unit time due to (three body) collisions between two atoms in presence of a third atom.

The fact that at a dissociative collision one molecule gets converted into two atoms and at a recombinative collision two atoms recombine to form one

molecule is used to relate the quantities (iii) to (vi) to quanties (ix) to (xii).

Thus we have

$$[f,f]_{dis} \quad = \quad \tfrac{1}{2} \{f,f\}_{dis}$$

$$\{f,F\}_{dis} \quad = \quad \tfrac{1}{2} \{f,f\}_{dis} \tag{5.1.3}$$

$$[F,F,f]_{recomb} \quad = \quad \tfrac{1}{3} \{F,F,f\}_{recomb}$$

$$[F,F,F]_{recomb} \quad = \quad \tfrac{1}{2} \{F,F,F\}_{recomb}$$

5.2. Dissociation and Recombination Rates :

The collisions resulting in dissociation and recombination may be represented by the following chemical formulae –

$$A_2 + A_2 \quad \underset{\text{recomb.}}{\overset{\text{dis}}{\rightleftharpoons}} \quad A_2 + A + A \tag{5.2.1}$$

$$A_2 + A \quad \underset{\text{recomb.}}{\overset{\text{dis}}{\rightleftharpoons}} \quad A + A + A \tag{5.2.2}$$

$$A_2 \quad \underset{\text{recomb.}}{\overset{\text{dis}}{\rightleftharpoons}} \quad A + A \tag{5.2.3}$$
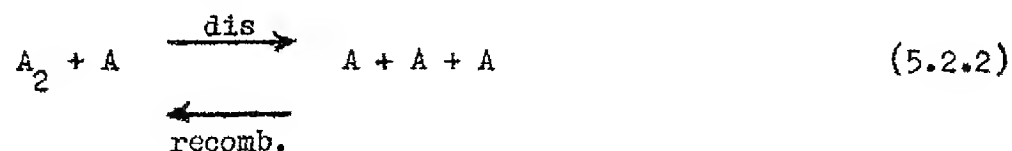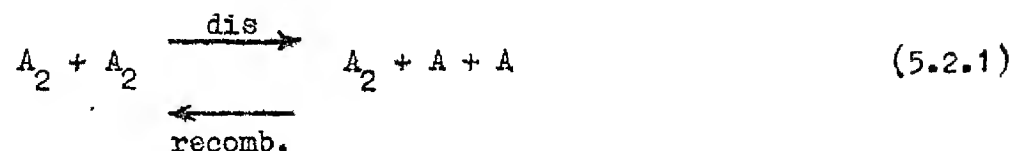
The probability of sufficiently strongly excited molecule dissociating into two atoms as indicated by forward reaction (5.2.3) (photo di socitation) is very small (Zeldovich, 1966). The same is true of the photo-recombination represented by reversed reaction (5.2.3). Hence these effects are neglected in this analysis.

The rate equations for the chemical reactions mentioned above may be written as

$$\left[\frac{dn_{A_2}}{dt}\right]_1 = -\frac{1}{2}\left[\frac{dn_A}{dt}\right]_1 = -k_{d_1}\, n_{A_2}^2 + k_{r_1}\, n_A^2\, n_{A_2} \tag{5.2.4}$$

$$\left[\frac{dn_{A_2}}{dt}\right]_2 = -\frac{1}{2}\left[\frac{dn_A}{dt}\right]_2 = -k_{d_2}\, n_{A_2}^2\, n_A + k_{r_2}\, n_A^3 \tag{5.2.5}$$

where n_A and n_{A_2} are the number densities of atoms and molecules respectively and the subscripts 1, 2 refer to the reactions in Eqn. (5.2.1) and Eqn. (5.2.2). The reaction rate constants may be related by the principle of detailed balancing as -

$$\frac{k_{d_1}}{k_{r_1}} = \frac{k_{d_2}}{k_{r_2}} = \left\{\frac{n_A^*}{n_{A_2}^*}\right\}^2 = K(T)$$

where $K(T)$ is the equilibrium constant; and n_A^* are $n_{A_2}^*$ equilibrium values of the number density of atoms and molecules at the given temperature. Thus, it suffices to know either the dissociation or the recombination rate.

5.2.1.   Calculation of the Dissociation Rate :

Dissociation is assumed to take place when a molecule collides with another molecule or an atom with sufficient energy. The frequency of inter - molecular collisions has already been calculated in Eqn. (3.4.3). The atom-molecule collision frequency has also been obtained as a special case of the inter-molecule collisions in Eqn. (3.4.4).

The fraction of collisions in which the total energy of the colliding partners exceeds the dissociation energy is given by Zeldovich (1966) as

$$\frac{1}{s_0!} \left(\frac{D}{RT}\right)^{s_0} \exp\left(-\frac{D}{RT}\right) \qquad\qquad (5.2.6)$$

where s_0 is a number characterising the degree of participation of the internal degrees of freedom in the dissociation process and D is the dissociation energy. The probability of dissociation at an energetic collision is known as steric factor and has to be used to write down the dissociation rate. Thus, the dissociation rate for the reaction Eqn. (5.2.1) may be written using Eqn. (3.4.3) and the above two factors as -

$$[f,f]_{dis} = P_0 \frac{1}{s_0!}\left(\frac{D}{RT}\right)^{s_0} e^{-\frac{D}{RT}} \int ff_1 \gamma(-\underline{g}.\underline{n}) K \, d\underline{n} \, d\tau \, d\tau_1 \qquad (5.2.7)$$

For the forward reaction (5.2.2) the dissociation rate may be written as

$$[f,F]_{dis} = P_1 \frac{1}{s_1!}\left(\frac{D}{RT}\right)^{s_1} e^{-\frac{D}{RT}} \int fF_1 \gamma(-\underline{g}_1.\underline{n}) K_1 \, d\underline{n} \, d\tau \, d\varsigma_1$$

where (P_0, s_0), (P_1, s_1) are the parameters of the molecule-molecule and molecule - atom collisions, respectively. Experimental values of these parameters are available in Stupochenko (1967) for nitrogen and oxygen.

5.2.2. <u>Calculation of the Recombination Rate:</u>

Recombination is assumed to occur when a collision between two atoms takes place in the presence of a third particle - either a molecule or an atom - which carries part of the bond energy. The forward reactions in Eqns. (5.2.1) and (5.2.2) correspond to dissociative collisions while the reversed directions refer to recombinative collisions.

The recombination rates for both the reactions are determined*by
Eqn. (5.2.6) using the principle of detailed balancing so that we have

$$[f,F,F]_{recomb} \approx \frac{1}{K(T)} \ [f,f]_{dis.} \ n_o^2/n$$

$$[F,F,F]_{recomb} \approx \frac{1}{K(T)} \ [f,F]_{dis.} \ n_o^2/n$$

(5.2.9)

Thus, all the collision terms on the right hand sides of the Boltzmann
equations (5.1.1) and (5.1.2) for the molecules and atoms, respectively,
are determined.

5.3. The Shock Structure Problem:

In order to determine the structure of a plane shock wave in a
dissociating diatomic gas it is now necessary to solve the Boltzmann
equations (5.1.1) and (5.1.2) subject to the shock boundary conditions.
As has been done in the foregoing chapters, a moment method will be used
to solve the Boltzmann equations. Further, the trimodal ansatz used
for the non-dissociating gas earlier, will again be used here for the
molecular distribution function. Mott-Smith's bimodal ansatz will be
used for the atoms. Thus, we write

$$f(\underline{c}) = w_1 \ f_1 + w_3 \ f_3 + w_4 \ f_4$$

$$F(\underline{c}_1) = w_6 \ F_1 + w_5 \ F_2$$

(5.3.1)

where f_i are the same Maxwellian distribution functions as defined
in Chapter 4 while the F_j are defined by

$$F_j(\underline{c}_1) = n_{o_j} \ (\frac{2\pi k T_{o_j}}{m})^{3/2} \ \exp \ \{- \frac{m(\underline{c}_1 - \underline{i} \ U_{o_j})^2}{2k \ T_{o_j}} \}$$

(5.3.2)

---

*Strictly speaking this is valid only for the equilibrium situation and it is an
approximation for the present case

in which $(n_{o_1}, U_{o_1}, T_{o_1})$ and n_{o_2} are the upstream and downstream parameters for the atomic species given by

$$n_{o_1} = 2\,\alpha_1\,n_1, \quad U_{o_i} = u_1, \quad T_{o_1} = T_1 \text{ and } n_{o_2} = 2\,\alpha_4\,n_4 \qquad (5.3.3)$$

and U_{o_2}, T_{o_2} are functions of the distance through the shock.

For the upstream temperatures upto $5000°C$ for nitrogen, the degree of dissociation is negligibly small so that for all practical purposes we may assume $\alpha_1 = 0$. Consequently the distribution function for the atoms becomes a Maxwellian

$$F(\underset{\sim}{c}_1) = 2w_5\alpha_4 n_4 \left(\frac{2\pi k T_{o_2}}{m}\right)^{3/2} \exp\left\{-\frac{m(c_1 - i\,U_{o_2})^2}{2k\,T_{o_2}}\right\} \qquad (5.3.4)$$

with the weight function w_5, temperature T_{o_2} and velocity U_{o_2} as the three unknowns in F. As the masses of a molecule and an atom are comparable the momentum and energy transfer (translational) is efficient at a collision. With this physical picture, the Temperature T_{o_2} and the velocity U_{o_2} for the atomic species are assumed to be same as that for the molecular species.

i.e. $T_{o_2} = T_t$ and $U_{o_2} = u$

where T_t and u are given by the Eqns. (4.5.1). Thus we have altogether 4 unknown weight functions w_i, $i = 1,3,4,5$ which have to be determined by the moment method. The distribution functions must satisfy the two species conservation equations obtained by using the trimodal ansatz of Eqn. (5.3.1) as

$$\sum_{i=1}^{4} n_i\,u_i\,\frac{dw_i}{dx} = \chi\left[\sum_{i=1}^{4}\sum_{j=1}^{4} w_i w_j\,D_{ij} + \sum_{i=1}^{4} w_i w_5\,D_{oi2}\right] = R_1$$

$$2\,\alpha_4\,n_4\,u_4\,\frac{dw_5}{dx} = -2R_1$$

where $(5.3.5)$

$$w_2 \quad 0, \quad D_{ij} \quad \int f_1, f_j]_{dis}\,d\tau, \quad D_{oi2} \quad \int f_1, \Gamma_2]_{dis}\,d\tau$$

$$2/n \qquad (5.3.6)$$

The integrals D_{ij}, $D_{o_{i_2}}$ have all been evaluated in Appendix C.

Two more moments of the Boltzmann equation for the molecules are chosen to obtain a complete set of 4 equations for the 4 unknowns. As in the case of non-dissociating molecules, we shall choose the rotational energy and vibrational energy the Boltzmann equation (5.1.1). The resulting moment equations may be written as : —

$$\sum_{i=1}^{4} n_i u_i k T_{r_i} \frac{dw_i}{dx} = \sum_{i,j=1}^{4} w_i w_j I_{ij} (\tfrac{1}{2} J_1 \omega_1^2) + \sum_{i=1}^{4} w_i w_5 I_{o_{i2}} (\tfrac{1}{2} J_1 \omega_1^2)$$

$$+ x \left[\sum_{i,j=1}^{4} w_i w_j R_{ij} (\tfrac{1}{2} J_1 \omega_1^2) + \sum_{i=1}^{4} w_i w_5 R_{o_{i2}} (\tfrac{1}{2} J_1 \omega_1^2) \right]$$

$$\sum_{i=1}^{4} n_i u_i k T_{v_i} \frac{dw_i}{dx} = \sum_{i,j=1}^{4} w_i w_j I_{ij} (\tfrac{1}{2} s (2B)^2) + \sum_{i=1}^{4} w_i w_5 I_{o_{i2}} (\tfrac{1}{2} s (2B)^2)$$

$$x \left[\sum_{i,j=1}^{4} w_i w_j R_{ij} (\tfrac{1}{2} s (2B)^2) \right.$$

$$\left. + \sum_{i=1}^{4} w_i w_5 R_{o_{i2}} (\tfrac{1}{2} s (2B)^2) \right] \tag{5.3.7}$$

where $I_{ij} (\Phi)$ are the collision integrals already defined in Chapter 4, and

$$R_{ij} (\Phi) = \int \Phi [f_i, f_1]_{dis} \, d\tau$$

$$R_{o_{i2}} (\Phi) = \int \Phi [f_i, f_2]_{dis} \, d\tau \tag{5.3.8}$$

$$w_2 = 0.$$

These integrals are also 22 fold, as in the earlier case and 16 fold integration are done analytically in Appendix C and the remaining integrations are carried out numerically using Monte Carlo technique given in Chapter 6.

From the foregoing discussion we obtain a set of 4 ordinary, coupled, non-linear, differential equations which must be solved simultaneously for the weight functions subject to the boundary conditions

$$w_1 = 1 \; ; \; w_3 = w_4 = w_5 = 0 \qquad \text{for } x \to -\infty$$
$$w_1 = w_3 = 0 \; ; \; w_4 = 1-\alpha_4, w_5 = 1 \quad \text{for } x \to \infty$$

$$(5.3.9)$$

The Eqns. (5.3.5) and (5.3.7) are solved numerically for these boundary conditions and shock profiles are obtained for a range of Mach numbers and three upstream pressures. The results thus obtained are discussed in Chapter 7.

CHAPTER - 6

NUMERICAL EVALUATION OF INTEGRALS

6.1   Introduction :

The collision integrals in the moment equations encountered in
the preceding two chapters are 22 fold and in most of the cases 16
fold integrations were carried out analytically.   It was not possible
to do the remaining 6 fold integration analytically and hence a numerical
approach was resorted to.   In any of the standard techniques of multiple
quadrature, the number of points required to evaluate an integral goes
up in geometrical progression as the order of the manifold integral.
This exponential increase never occurs in case of Monte Carlo evaluation.
Thus for the numerical integration of manifold integrals this method is
very economical.   The Monte Carlo technique gives a reasonable estimate
of the integral and errors in the integration can also be estimated during
the process of integration.

6.2.   Monte Carlo Integration :

A typical integral which has to be evaluated may be written
formally from Appendix A or C as

$$ I = \int_0^{2\pi} d\phi \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\beta \int_0^{\pi} d\beta_1 \int_0^{B_{max}} dB \int_0^{B_{max}} F(B,B_1,\phi,\phi_1,\beta,\beta_1) \ dB_1 \qquad (6.2.1) $$

For a Monte Carlo evaluation of this integral the limits of integration
are changed to 0 to 1 for all the variables by using linear transformations
for then.   Thus we have the integral

$$I = \int_0^1 dx \int_0^1 dy \int_0^1 dz \int_0^1 du \int_0^1 dv \int_0^1 \quad H(x,y,z,u,v,w) \quad dw \qquad (6.2.2)$$

where

$$H(x,y,z,u,v,w) = 4\pi^4 \, B_{max}^2 \, F(B,B_1,\phi,\phi_1,\beta,\beta_1) \qquad (6.2.3)$$

The method consists of evaluating the integrand H at N randomly chosen points $(x_i, y_i, z_i, u_i, v_i, w_i)$, $i = 1, N$ lying with-in the domain of region of integration and finding average of these N values. This average value itself is an estimate I_{eN} of the integral.

i.e. $$I \simeq I_{eN} = \frac{1}{N} \sum_{i=1}^{N} H(x_i, y_i, z_i, u_i, v_i, w_i) \qquad (6.2.4)$$

For this calculation the points $(x_i, y_i, z_i, u_i, v_i, w_i)$ are chosen as random numbers belonging to 6 independent series of uniformly distributed random numbers between 0 to 1. For the numerical computational purposes the random digits available in the Rand Corporation Table have been used in this thesis.

6.3 Error Estimation :

The variance of H is defined by

$$\sigma^2 = \int_0^1 (H-I)^2 \, d\tau = \overline{H^2} - I^2 \qquad (6.3.1)$$

where

$$d\tau = dx \, dy \, dz \, du \, dv \, dw, \quad \overline{H^2} = \int_0^1 H^2 \, d\tau \qquad (6.3.2)$$

and the standard deviation S_o is given by

$$S_o = \sigma / \sqrt{N} \qquad (6.3.3)$$

the estimation of integral I, then a $\pm$ 15% error in this error
estimation allows the overall error in I to take a value between
8.5% and 11.5%.

In pratical calculations the choice of N depends on the error
that can be allowed. Lordi and Mates (1970) evaluated 6 fold
integrals encountered in their analysis, using Monte Carlo technique
and obtained satisfactory estimates for the multi-dimensional integrals.
They used 400-500 trials for different cases depending on the error
criterion. Three typical plots of the estimates I_{eN} and S_{oeN} versus
N are given in Fig. (6.3.1) for the case of three collision integrals
for c_x^2, Rotational Energy and Vibrational Energy. It is found that
600 trials are required to limit the overall error to $\pm$ 10% in the
last two cases. However, for the c_x^2 moment integral as many as 1000
trials were necessary to restrict the error to $\pm$ 10%. In a few cases
of the c_x^2 moment integrals, the errors were as high as 26% for 1000
trials.

For evaluating a typical six fold integral $I_{ij}(\phi)$ or $D_{ij}(\phi)$ or $R_{ij}(\phi)$
given in Appendix A or C it takes about 3 minutes on the IBM 7044,
with 600 Monte Carlo trials. For the cases when $i \neq j$, the integrals
are 7 fold and the same procedure is adopted for evaluating this
integral. The computer time taken for these cases is about $3\frac{1}{2}$ minutes.

As the integrations are carried out approximately the shock profiles
calculated may also be expected to be approximate to the same extent.
In the next, chapter a discussion on the results and conclusions are
given.

CHAPTER 7

DISCUSSIONS AND CONCLUSIONS

7.1. Shock Structure in a Vibrationally Relaxing Gas

An attempt was made in Chapter 4 to investigate the effects of vibrational relaxation on the structure of a shock wave and two formulations were presented for diatomic gases. Both the trimodal and the quadrimodal theories are extensions of the Mott Smith bimodal approach and the trimodal theory of Haight for a rotationally relaxing diatomic gas. The various shock profiles for nitrogen predicted by the trimodal theory of Chapter 4 are shown in Figs. 7.1.1 to 16 and the results given by the quadrimodal approach are presented in Figs. 7.2.1 to 9.

7.1.1. Shock Profiles (Trimodal Theory): The trimodal calculations are carried out for the upstream Mach numbers ranging from 12 to 30 ar for the upstream pressures of 0.1, 0.01 and 0.001 atmosphere. The density profiles for these Mach numbers are given in Figs. 7.1.1 to 6 It is seen from these profiles that for a given upstream Mach number the shock transition takes place faster with the decrease of the upstream pressure, whereas for a given upstream pressure the shock becomes thinner with the increase of the upstream Mach number.

The corresponding temperature profiles are given in Figs. 7.1. to 12. The dependence of the width of the zone of temperature varia on the free-stream conditions, is same as in the case of density. In all the cases, the translational temperature initially rises at a fas rate to a maximum and then decreases gradually to its down-stream equilibrium value, thus exhibiting a pronounced temperature peak. The

the rotational profile lags behind the translational one, it shows a peak
for Mach numbers above 20.   This overshoot is very much less pronounced
and it occurs slightly later when compared to that of translational
temperature.   However the vibrational temperature monotonically increases
to its down-stream equilibrium value and further it is found to lag behind
the other two temperatures.   This lag in the vibrational temperature is
significant for Mach numbers above 20.

The above pattern of the three temperature distributions may be
explained as follows: The translational degrees being the fastest of
the three, the corresponding temperature attains its equilibrium value
(monatomic) first with-in a short distance $(\sim \lambda_1)$.   This is also true
of the rotational degrees of freedom which is slower than the translational
but faster than the vibrational degrees of freedom.   Finally the slowest
of the three namely the vibrational degree absorb energy from the faster
ones and relax to the equilibrium state gradually.   The degree of lag of
vibrational temperature at lower Mach numbers is small mainly due to the
classical nature of the vibrational mode assumed.

In Figs. 7.1.13 and 14 are shown the density and temperature
profiles with the upstream temperature as a parameter.   It is seen from
these profiles that for a given M_1, an increase in the upstream temperature
reduces the extent of the shock due to higher absolute temperatures inside
the shock.

A typical variation of the weight functions w_1, w_3 and w_4 is given
in Fig. 7.1.15.   The functions w_1 and w_4 show a monotonic behaviour
within the shock, whereas w_3, as expected has a maximum inside the
shock with zero values at the two ends.   For $M_1 > 20$, w_3 is found to
take small values.   This fact is reflected in the non-existence of a peak

in the rotational temperature and a faster approach of the vibrational temperature to the rotational temperature.   This is perhaps attributable to the lower population of the molecules characterised by f_3 inside the shock, as the down-stream condition (f_4) is attained faster due to the classical behaviour of the vibrational degrees of freedom assumed.   This is not so at higher Mach numbers as this assumption regarding the vibration degrees of freedom is valid to a better extent.

A comparision of the theoretical profiles with the experimental sh profiles given by Robben and Talbot (1966) is made in Fig. 7.1.16 for $M_1 = 12.9$.   The density profile predicted by the trimodal theory compare very well with the experimental profiles over more than half the distance through the shock and differ slightly over rest of the distance.   But for a shift in the calculated rotational temperature profile, it also compares very well with the experimental profile.

7.1.2   Shock Profiles (Quadrimodal Theory): The density profiles for the quadrimodal case are given in Figs. 7.2.1 to 3 and the temperature profiles in Figs. 7.2.4 to 6. The calculations were done for $M_1 = 15$, 20 and 25 and for the upstream pressures indicated earlier. (For $M_1 = 30$, the shock profile are obtained at $p_1 = 0.1$ atmosphere and are shown in Fig. 7.2.7.)   The profiles in this case are qualitatively same as in the trimodal case.   The translational temperature overshoots are some what higher in this case than for the earlier theory.

In Fig. 7.2.9 a comparison of the various profiles given by both the theories is made (while comparing $\tilde{\rho} = 0.5$ is matched for both the cases where $\tilde{\rho} = (\rho - \rho_1) / (\rho_4 - \rho_1)$.   The density profiles match closely upto a certain distance from the upstream whereas, the temperature profile compare fairly closely but for the over shoot in $\bar{T}_t$.   Fig. 7.2.8 shows a typical   tion of the weight functions w_1.   The functions w_1 and w_4

have monotonic behaviour as in the earlier case and w_2 and w_3 possess a maximum within the shock, having zero values at the two ends.

7.1.3. Shock Thickness: The following three shock thicknesses are calculated for the vibrationally relaxing diatomic gas using the profiles given by both the theories: density thickness (Δ_ρ), vibrational tempera-.ure thickness (Δ_V) and the rotational temperature thickness (Δ_R). In all the cases the maximum slopes of the corresponding profiles are used. These thickness indicate the extent of the shock when the actual profiles are replaced by linear profiles with the corresponding maximum slopes. The variation of the reciprocal shock thicknesses with the upstream Mach number is shown in Figs. 7.4.1 to 3. For nondimensionalising the shock thickness a length L* adopted by Robben and Talbot (1966) is used instead of the free-stream λ_1 . It is seen from the figures that the density thickness is lower than the two temperature thicknesses at higher Mach numbers.This is expected due to the presence of the rotational and vibrational relaxation zones at higher Mach numbers. The quadrimodal approach predict lower values for the shock thicknesses. The experimental values of Δ_ρ and Δ_R at $M_1 = 12.9$ given by Robben and Talbot (1966) are also shown for comparision. The theoretical Δ_R compares well with the experimental value at $M_1 = 12.9$. Finally, for a given M_1 the shock thicknesses are found to decrease with the upstream pressure.

7.2. Shock Structure in a Dissociating Diatomic Gas:

The analysis given in Chapter 4 was further extended to include the effects of dissociation in Chapter 5. The shock profiles thus obtained are presented in Figs. 7.3.1 to 9.

7.2.1. Shock Profiles with Dissociation Effects: In Figs. 7.3.1 to 3 the degree of dissociation, total density and molecular density profiles are given for M_1 15, 20 and 25 respectively. The profiles are also given

for $M_1 = 25$ with p_1 as parameter in Fig. 7.3.4. The corresponding temperature profiles are given in Figs. 7.3.5 to 8. In all these profiles the total density is found to increase monotonically whereas the molecular density has a maximum inside the shock. The difference of these densities is related to the degree of dissociation by $\alpha = 1 - \rho_m/\rho$ The study made by Dorrance (1961) indicates the possibility of maxima for both ρ and α. However in the present case inspite of a peak in the profiles for ρ_m, the profiles for degree of dissociation have a monotonic behaviour.

For a low α (~ 0.2) the three temperatures T_t, T_r and T_v are found to equilibrate in a narrow region where the dissociation is practically absent. This region is followed by a very broad clearly distinguishable tail in which the degree of dissociation attains its equilibrium value. In this broad region the changes in ρ, T_t, T_r and T_v are very gradual whereas the molecular density and the degree of dissociation change significantly (see Fig. 7.3.1, 2, 5 and 6).

For a high α ($\sim .9$) the two regions lose their identity and merge together. However there exists a broad zone in which the three temperatures attain nearly their equilibrium value. This is followed by a tail whose width is also of the same order. In this region the only quantities which vary significantly are the two densities and the degree of dissociation. (see Figs. 7.3.3 and 7).

Finally for a moderately high α (~ 0.6) there exists a broad region in which the three temperatures and the total density attain almost their equilibrium value. This is followed by a very broad region in which the molecular density and the degree of dissociation attain their equilibrium values as in the case of low α. In otherwords the

merger of the two zones will have just begun. (see Figs. 7.3.4 and 8).
These figures also indicate the effects of the upstream pressure p_1
on the various profiles. As found in the case of shock structure without
dissociation, in this case also, with the decrease of p_1 the extent of the
shock decreases.

7.2.1. Shock Thickness with Dissociation Effects: The definition of
shock thickness should have some bearing to the kind of relaxation
phenomena predominent. For the shock in dissociating gas the degree of
dissociation of the gas has to be incorporated in the definition of a
thickness. For the present case in the absence of any other definition
in the literature, a shock thickness Δ is defined as a distance from
the begining of the shock transition to a point inside the shock where
the degree of dissociation is 90 % of the down-stream equilibrium value.
(A similar definition has been adopted in the case of ionising shock
waves in monotonic gases). The position where shock transition starts
is of course not very well defined and to this extent there is certain
amount of arbitrariness in the value of Δ chosen.

For a given upstream pressure the equilibrium degree of dissoci-
ation increases with the Mach number. Further with the increase of
equilibrium degree of dissociation the shock thickness decreases. This
fact is reflected in Fig. 7.4.4 which shows the variation of Δ and
$1/\Delta$ with M_1 for nitrogen

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7.3. Conclusions :

For the comparison purposes hardly any experimental shock profile data for nitrogen in the Mach number range considered is available. Thus no definite conclusion can be made as to the validity of the theory. However the two formulations—quadrimodal and trimodal—given in Chapter 4 are capable of predicting the shock structure in a vibrationally relaxing diatomic gas. Out of these two, the quadrimodal theory is better than the trimodal one especially for the Mach number range 15 to 20. Further the analysis presented in Chapter 5 includes the dissociation effects in the gas and hence is valid for higher Mach numbers upto 30. For $M_1 > 30$, the ionisation and photo-recombination of the atoms and photo-dissociation of the molecules become appreciable. These effects are not included in the present formulation.

As particular cases of the quadrimodal theory, for vibrationally relaxing diatomic gas given in Chapter 4, it is possible to recover, both the trimodal theory proposed by Haight for rotationally relaxing diatomic gases $(w_4=0)$ and the Mott Smith bimodal theory $(w_3=w_4=0)$ for inert gases.

Further to enable to carryout meaningful calculations for shock structure, the parameters b, a and s for axially elastic spherocylinder models corresponding to real diatomic gas molecules should be available. In the present case the values indicated in the Table 2.1.1 were used.

The shock structure analysis given in Chapter 5 for the dissociating gas may further be extended for a mixture of atoms and molecules of the same gas. In such a case the upstream atomic number density is nonzero and hence the full bimodal ansatz for the distribution function for atoms has to be retained. Correspondingly, appropriate number of relevant moments of the two Boltzmann equations have to be considered in addition to the equations of Chapter 5.

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APPENDIX - A

COLLISION INTEGRALS $I_{ij}(\Phi)$

The collision integrals in the moment equations are given by

$$I_{ij}(\phi) = - \int (\phi_1' - \phi' - \phi_1 - \phi) f_i f_{j1} \; \gamma(-g.n) K \; dn \; d\tau \; d\tau_1 \qquad (A.1.1)$$

where

$$g.n = \{(c_1 + \omega_1 \times r_1 - B_1 \, v \, \sin \phi_1 \, e_1)$$

$$- (c + \omega \times r - B \, v \, \sin \phi \, e)\}. \; n$$

$K \; dn$ elemental area on the interaction surface and $\gamma(x) = 0$ for $x < 0$, $= 1$ for $x > 0$.

From the dynamics of binary collision (Chapter 2) we have for the impulse I transmitted at a collision from molecule 1 to molecule 2

$$I = - \frac{g.n}{\zeta/m} \qquad (A.1.3)$$

where

$$\zeta = 1 + \frac{m}{2I_1} \{(b+B \cos \phi)^2 (e \times n)^2 + (b+B_1 \cos \phi_1)^2 (e_1 \times n)^2 \qquad (A.1.4)$$

Further the post collision variables are given by the following equations

$$c_1' = c_1 + \frac{I}{m} \, n \; ; \; c' = c - \frac{I}{m} \, n$$

$$\omega_1' = \omega_1 + \frac{I}{J_1} \, (b + B_1 \cos \phi_1) \, (e_1 \times n) \qquad (A.1.5)$$

$$\omega = \omega - \frac{I}{J_1} \, (b + B \cos \phi) \, (e \times n)$$

The collision integral given by Eqn. (A.1.1) is a 22 fold integral. Without making a particular choice for $\phi(c_x^2, 1/2\ J_1\ \omega_\perp^2$ or $1/2\ s(2B)^2)$ it is possible to carry out 11 integrations analytically. The dependence of the integrand on $\underset{\sim}{e}$, $\underset{\sim}{e}_1$, $\underset{\sim}{n}$, $\underset{\sim}{\omega}$ and $\underset{\sim}{\omega}_1$ is limited to the following combination of them:

$\underset{\sim}{e}\cdot\underset{\sim}{n}$, $\underset{\sim}{e}_1\cdot\underset{\sim}{n}$, $\underset{\sim}{e}\times\underset{\sim}{e}_1\cdot\underset{\sim}{n}$, $\underset{\sim}{\omega}\cdot\underset{\sim}{e}(\omega_{\parallel})$, $\underset{\sim}{\omega}_1\cdot\underset{\sim}{e}_1(\omega_{1\parallel})$, $\underset{\sim}{\omega}\cdot\underset{\sim}{e}\times\underset{\sim}{n}$

and $\underset{\sim}{\omega}_1\ \underset{\sim}{e}_1\times\underset{\sim}{n}$.

Thus the vectors $\underset{\sim}{\omega}$ and $\underset{\sim}{\omega}_1$ may be expressed in terms of $\underset{\sim}{e}$, $\underset{\sim}{e}_1$ and $\underset{\sim}{n}_1$ as follows (see Fig. A.1.1), for facilitating the integrations in $\underset{\sim}{\omega}$ and $\underset{\sim}{\omega}_1$ space. In such a case we have

$$\underset{\sim}{\omega} = \omega\{\underset{\sim}{e}\cos\theta + (\frac{\underset{\sim}{e}\times\underset{\sim}{n}}{|\underset{\sim}{e}\times\underset{\sim}{n}|}\cos\psi + \underset{\sim}{e}\times\frac{\underset{\sim}{e}\times\underset{\sim}{n}}{|\underset{\sim}{e}\times\underset{\sim}{n}|}\sin\psi)\sin\theta\}$$

$$\underset{\sim}{\omega}_1 = \omega_1\{\underset{\sim}{e}_1\cos\theta_1 + (\frac{\underset{\sim}{e}_1\times\underset{\sim}{n}}{|\underset{\sim}{e}_1\times\underset{\sim}{n}_1|}\cos\psi_1 + \underset{\sim}{e}_1\times\frac{\underset{\sim}{e}_1\times\underset{\sim}{n}}{|\underset{\sim}{e}_1\times\underset{\sim}{n}|}\sin\psi_1)\sin\theta_1\}$$

(A.1.6)

$$\omega_{\parallel} = \omega\sin\theta \ , \ \omega_{1\parallel} = \omega_1\sin\theta_1$$

$$d\underset{\sim}{\omega} = \omega^2\sin\theta\ d\omega\ d\theta\ d\psi = \omega_\perp\ d\omega_\perp\ d\omega_{\parallel}\ d\psi$$

and

$$d\underset{\sim}{\omega}_1 = \omega_1^2\ \sin\theta_1\ d\omega_1\ d\theta_1\ d\psi_1 = \omega_{1\perp}\ d\omega_{1\perp}\ d\omega_{1\parallel}\ d\psi_1$$

Further representing $\underset{\sim}{e}$ and $\underset{\sim}{e}_1$ in spherical co-ordinates we get

$$\underset{\sim}{e} = \underset{\sim}{n}\cos\beta + \{\frac{\underset{\sim}{n}\times\underset{\sim}{e}_1}{\underset{\sim}{n}\times\underset{\sim}{e}_1}\cos\epsilon + \underset{\sim}{n}\ \frac{\underset{\sim}{n}\times\underset{\sim}{e}_1}{\underset{\sim}{n}\times\underset{\sim}{e}_1}\sin\epsilon\}\sin\beta$$

$$\underset{\sim}{e}_1 = \underset{\sim}{n}\cos\beta_1 + (\underset{\sim}{s}\cos\epsilon_1 + \underset{\sim}{t}\sin\epsilon_1)\sin\beta_1$$

$$d\underset{\sim}{e} = \sin \beta \ d\beta \ d\epsilon$$

and (A.1.7)

$$d\underset{\sim}{e}_1 = \sin \beta_1 \ d\beta_1 \ d\epsilon_1$$

where $\underset{\sim}{s}$, $\underset{\sim}{t}$ and $\underset{\sim}{n}$ form an orthogonal set. Consequently we have the following relationships useful for the integration

$$\underset{\sim}{e} \cdot \underset{\sim}{n} = \cos \beta \ ; \ \underset{\sim}{e}_1 \cdot \underset{\sim}{n} = - \cos \beta_1,$$

$$\underset{\sim}{e} \times \underset{\sim}{e}_1 \cdot \underset{\sim}{n} = - \sin \beta \sin \beta_1 \cos \epsilon \qquad (A.1.8)$$

$$\underset{\sim}{\omega} \cdot \underset{\sim}{e} \times \underset{\sim}{n} = \omega \sin \theta \cos \psi \sin\beta$$

and

$$\underset{\sim}{\omega}_1 \cdot \underset{\sim}{e}_1 \times \underset{\sim}{n} = \omega_1 \sin \theta_1 \cos \psi_1 \sin \beta_1$$

Using these relationships we can rewrite Eqns. (A.1.2) and (A.1.4) as

$$\underset{\sim}{g} \cdot \underset{\sim}{n} = \underset{\sim}{v} \cdot \underset{\sim}{n} + (b+B_1 \cos \phi_1) \ \omega_{1\perp} \cos \psi \sin \beta_1 - (b + B \cos \psi) \ \omega_\perp \cos \psi$$

$$\times \sin \beta + v (B_1 \sin \phi_1 \cos \beta_1 - B \sin \phi \cos \beta) \qquad (A.1.9)$$

$$\zeta = 1 + \frac{mb^2}{2J_1} \{(1+\overline{B}_1 \cos \phi_1)^2 \sin^2\beta_1 + (1+\overline{B} \cos \phi)^2 \sin^2 \beta\} \qquad (A.1.10)$$

where

$$\underset{\sim}{v} = \underset{\sim}{c}_1 - \underset{\sim}{c} \qquad (A.1.11)$$

Now the integrations with respect to ϵ and ϵ_1 may be carried out, as the dependence on them is only through K. Thus we have

$$\int K \ d\epsilon \ d\epsilon_1 = (2\pi)^2 \ \overline{K} \qquad (A.1.12)$$

where

$$\bar{B} = B/b \ , \ \bar{B}_1 = B_1/b$$

and

$$\bar{K} = 4a^2 \ [1+2 \ \frac{b}{a}\{(1+\bar{B} \ \cos \ \phi)\delta(\cos \ \beta)\sin^2 \ \beta \ + \ (1+\bar{B}_1 \ \cos \ \phi_1)\delta(-\cos \ \beta_1)$$

$$\sin^2\beta_1\}+(\frac{b}{a})^2(1+\bar{B} \ \cos \ \phi)(1+\bar{B}_1 \ \cos \ \phi_1)\sin^2\beta \ \sin^2\beta_1\delta(\cos \ \beta)\delta(-\cos \ \beta)]$$

$$(A.1.13)$$

In the integrand, $\underset{\sim}{n}$ appears through the term $\underset{\sim}{v}\cdot\underset{\sim}{n}$. Representing $\underset{\sim}{n}$ interms $\underset{\sim}{v}$ and $\underset{\sim}{i}$ we get

$$\underset{\sim}{n} = \frac{\underset{\sim}{v}}{v} \ \cos \ \alpha \ + \ \{\frac{\underset{\sim}{v}\times\underset{\sim}{i}}{|\underset{\sim}{v}\times\underset{\sim}{i}|} \ \cos \ \delta \ + \ \frac{\underset{\sim}{v}}{v} \times \ \frac{\underset{\sim}{v}\times\underset{\sim}{i}}{|\underset{\sim}{v}\times\underset{\sim}{i}|} \ \sin \ \delta\} \ \sin \ \alpha$$

$$(A.1.14)$$

$$\underset{\sim}{v}\cdot\underset{\sim}{n} = v \ \cos \ \alpha$$

and

$$d\underset{\sim}{n} = \sin \ \alpha \ d\alpha \ d\delta$$

The dependence of the integrand on δ if any is only through $\{\bar{\phi}\}$ and we can write, at this state

$$\int_0^{2\pi} \{\phi\} \ d\delta \ = \ 2\pi \ \overline{\{\phi\}} \qquad\qquad (A.1.15)$$

Thus we have the collision integral given by Eqn. (A.1.1) as.

$$I_{ij}(\phi) = -(2\pi)^3 \ \int \overline{\{\phi\}} \qquad \sqrt{(-\underset{\sim}{g}\cdot\underset{\sim}{n})f_if_{j1}} \ \bar{K} \ \sin \ \alpha \ d\alpha \ d\bar{\tau} \ d\bar{\tau}_1 \qquad (A.1.16)$$

where

$$d\overline{\tau} = bd\ \underset{\sim}{c}\ \omega_{\perp}d\omega_{\perp}\ d\omega_{\text{II}}\ d\psi\ \sin\ \beta\ d\beta\ d\overline{B}\ d\ \phi$$

$$d\overline{\tau}_1 = b\ d\underset{\sim}{c}_1\ \omega_{1\perp}\ d\omega_{1\perp}\ d\omega_{1\text{II}}\ d\psi_1\ \sin\ \beta_1\ d\beta_1\ d\overline{B}_1\ d\phi_1 \qquad (A.1.17)$$

and

$$f_p = \frac{n_p}{8\pi^2}\ \left(\frac{m}{2\pi kT_{t_p}}\right)^{3/2}\ \left(\frac{J_1}{2\pi kT_{r_p}}\right)\ \left(\frac{8s}{\pi kT_{v_p}}\right)^{1/2}\ \exp\ \{-\ \frac{m(\underset{\sim}{c}\ -\ u_p\ \underset{\sim}{i})^2}{2kT_{t_p}}$$

$$-\ \frac{J_1\ \omega_{\perp}^2}{2kT_{r_p}}\ -\ \frac{s(2B)2}{2kT_{v_p}}\}\ F(\omega_{\text{II}}) \qquad (A.1.18)$$

in which $F(\omega_{\text{II}})$ satisfies the following condition

$$\int_{-\infty}^{\infty}\ F(\omega_{\text{II}})\ d\omega_{\text{II}} = 1. \qquad (A.1.19)$$

By using this (A.1.19) two trivial integrations with respect to ω_{II}
and $\omega_{1\text{II}}$ may be carried out straight away.

The integrations in the velocity space $\underset{\sim}{c}$, $\underset{\sim}{c}_1$ may be carried
out by using the standard transformations

$$\underset{\sim}{c} = u_i\ \underset{\sim}{i}\ +\ \underset{\sim}{V}\ -\ \underset{\sim}{G}\ \frac{T_{ti}}{T_{ti} + T_{tj}}$$

$$\underset{\sim}{c}_1 = u_j\ \underset{\sim}{i}\ +\ \underset{\sim}{V}\ +\ \underset{\sim}{G}\ \frac{T_{tj}}{T_{ti} + T_{tj}} \qquad (A.1.20)$$

such that

$$d\ \underset{\sim}{c}\ d\ \underset{\sim}{c}_1\ = d\ \underset{\sim}{V}\ d\ \underset{\sim}{G} \qquad (A.1.21)$$

By inspection it can easily be seen that integrand is dependent
on $\underset{\sim}{V}$ only through the exponential term. Thus performing the
integrations in $\underset{\sim}{V}$ space we get the collision integral given by
Eqn. (A.1.17) as

$$I_{ij}(\phi) = -(2\pi)^3 \frac{n_i n_j}{(8\pi^2)^2} \left\{\frac{m}{2\pi k (T_{t_i} + T_{t_j})}\right\}^{3/2} \left\{\frac{J_1}{2\pi k T_{r_i}}\right\} \left\{\frac{J_1}{2\pi k T_{r_j}}\right\}$$

$$\left(\frac{8s}{\pi k T_{v_i}}\right)^{1/2} \left(\frac{8s}{\pi k T_{v_j}}\right)^{1/2} b^2 \, f(\phi) \, (\underset{\sim}{g} \cdot \underset{\sim}{n}) \, \gamma(-\underset{\sim}{g} \cdot \underset{\sim}{n}) \, \exp \left\{-\frac{mG^2}{2k \, (T_{t_i} + T_{t_j})}\right.$$

$$\left. -\frac{J_1 \omega_\perp^2}{2kT_{r_i}} - \frac{J_1 \omega_{1\perp}^2}{2kT_{r_j}} - \frac{s(2B)^2}{2kT_{v_i}} - \frac{s(2B)^2}{2kT_{v_j}}\right\} \, \overline{K} \, \sin \alpha \, d\alpha \, d\tau' \, d\overline{\tau}_6 \qquad (A.1.22)$$

where

$$d\tau' = d\underline{G} \, \omega_\perp d\omega_\perp \, d\psi \, \omega_{1\perp} \, d\omega_{1\perp} \, d\psi_1$$

$$\qquad\qquad\qquad (A.1.23)$$

$$d\overline{\tau}_6 = \sin \beta \, \sin \beta_1 \, d\overline{\epsilon} \, d\overline{\epsilon}_1 \, d\phi \, d\psi_1 \, d\beta \, d\beta_1$$

and the following result is used

$$\int \exp \left\{-\frac{m}{2k} \frac{T_{t_i} + T_{t_j}}{T_{t_i} T_{t_j}} \underset{\sim}{V}^2\right\} \, d\underset{\sim}{V} = \left\{\frac{2\pi k}{m} \frac{T_{t_i} T_{t_j}}{T_{t_i} + T_{t_j}}\right\}^{3/2} \qquad (A.1.24)$$

Further transforming $(\omega_\perp, \psi)$ and $(\omega_{1\perp}, \psi_1)$ to a cartesian co-ordinates, after suitably non-dimensionalising them we have

$$\omega_\perp \, d\omega_\perp \, d\psi = \frac{2k \, T_{r_i}}{J_1} \, d\overline{\omega}_x \, d\overline{\omega}_y$$

$$\qquad\qquad\qquad (A.1.25)$$

$$\omega_{1\perp} \, d\omega_{1\perp} \, d\psi_1 = \frac{2k \, T_{r_j}}{J_1} \, d\overline{\omega}_{1x} \, d\overline{\omega}_{1y}$$

where

$$\overline{\omega}_x = \sqrt{\frac{J_1}{2kT_{r_i}}} \, \omega_\perp \, \cos \psi, \quad \overline{\omega}_y = \sqrt{\frac{J_1}{2k \, T_{r_i}}} \, \omega_\perp \, \sin \psi$$

$$\qquad\qquad\qquad (A.1.26)$$

$$\overline{\omega}_{1x} = \sqrt{\frac{J_1}{2k \, T_{r_j}}} \, \omega_{1\perp} \, \cos \psi_1, \quad \overline{\omega}_{1y} = \sqrt{\frac{J_1}{2k \, T_{r_j}}} \, \omega_{1\perp} \, \sin \psi_1$$

It can be easily seen that the integrand depends on $\bar{\omega}_x$ and $\bar{\omega}_{1y}$ through only the exponential terms which may be integrated by using the following well known integral

$$\int_{-\infty}^{\infty} e^{-\bar{\omega}_y^2} \, d\bar{\omega}_y = \sqrt{\pi} \tag{A.1.27}$$

Finally we use the following transformation for $\bar{\omega}_{;x}$ and $\bar{\omega}_{1x}$.

$$\eta = (b+B \cos \phi)\sqrt{\frac{2k \, T_{r_i}}{J_1}} \, \bar{\omega}_x \sin \beta - (b+B_1 \cos \phi_1)\sqrt{\frac{2k \, T_{r_j}}{J_1}} \, \bar{\omega}_{1x} \sin \beta_1$$

$$Z = (b+B_1 \cos \phi_1)\sqrt{\frac{2k \, T_{r_j}}{J_1}} \, \bar{\omega}_x \sin \beta_1 - (b+B \cos \phi)\sqrt{\frac{2k \, T_{r_i}}{J_1}} \, \bar{\omega}_{1x} \sin \beta \tag{A.1.28}$$

such that

$$\bar{\omega}_x^2 + \bar{\omega}_{1x}^2 = J(\eta^2 + Z^2) \; ; \; d\bar{\omega}_x \, d\bar{\omega}_{1x} = J^{-1} \, d\eta \, dZ$$

where the Jocobian of transformation is given by

$$J = \{(b+B \cos \phi)^2 \, \frac{2k \, T_{r_i}}{J_1} \sin^2 \beta + (b+B_1 \cos \phi_1)^2 \, \frac{2k \, T_{r_j}}{J_1} \sin^2 \beta_1\} \tag{A.1.29}$$

As the dependence of the integrand on Z is only through an exponential term, the Z integration can be performed using the standard result

$$\int_{-\infty}^{\infty} e^{-Z^2/J} \, dZ = \sqrt{\pi J} \tag{A.1.30}$$

Thus we have for any $\phi(c_x^2, \, 1/2 \, J_1 \, \omega_\perp^2 \text{ or } \frac{s(2B)^2}{2})$ the collision integral given by the 11 fold integral as follows

$$I_{ij}(\phi) = \cdot \frac{n_i n_j}{\pi^{3/2}} \left\{ \frac{m}{2\pi k (T_{t_i} + T_{t_j})} \right\}^{3/2} \left(\frac{8s}{\pi k \, T_{v_i}} \right)^{1/2} \left(\frac{8s}{\pi k \, T_{v_j}} \right)^{1/2} b^2$$

$$\int \overline{(\phi)} \; (\underset{\sim}{g} \cdot \underset{\sim}{n}) \; \gamma(-\underset{\sim}{g} \cdot \underset{\sim}{n}) \; \exp \left\{ - \frac{mG^2}{2k(T_{t_i} + T_{t_j})} - \overline{n}^2 - \frac{s(2B)^2}{2k \, T_{v_i}} \right.$$

$$\left. - \frac{s(2B_1)^2}{2k \, T_{v_j}} \right\} \; \overline{K} \sin \alpha \; d\alpha \; d\underset{\sim}{G} \; d\overline{\eta} \; d\overline{\tau}_6 \tag{A.1.31}$$

where

$$\overline{\eta} = \eta/\sqrt{J}$$

$$\underset{\sim}{g} \cdot \underset{\sim}{n} = v \cos \alpha - \eta + X \tag{A.1.32}$$

$$X = -v(B_1 \sin \phi_1 \cos \beta_1 - B \sin\phi \cos \beta)$$

There are yet 11 fold of integrations which are to be carried out. These can be done only after a particular choice is made for ϕ .

A.2.1 $\phi = c_x^2$:

Using the Eqns. (A.1.5) we can write

$$\{c_x^2\} = 2 \, v_x \frac{p_x}{\mu} \, I + 2I^2 \; \frac{n_x^2}{m^2} \tag{A.2.1}$$

where

$$n_x = \underset{\sim}{i} \cdot \underset{\sim}{n} = \frac{v_x}{v} \cos \alpha - \sqrt{\frac{v^2 - v_x^2}{v^2}} \sin \delta \sin \alpha$$

$$v_x = \underset{\sim}{i} \cdot \underset{\sim}{v} = c_{1x} - c_x \tag{A.2.2}$$

Eqns. (A.1.11) and (A.1.14) are used in writing down the Eqns. (A.2.2). As mentioned the dependence on δ is only through $\{c_x^2\}$ and the integration with respect to δ is carried out as follows (Use Eqn. (A.1.15))

$$2\pi \; \overline{\{c_x^2\}} = \int_0^{2\pi} \{c_x^2\} \; d\delta \tag{A.2.3}$$

Substituting from Eqns. (A.2.1) and (A.2.2) in (A.2.3) we get

$$\overline{\{c_x^2\}} = \frac{2I}{m} \frac{v_x^2}{v} \cos \; \alpha \; + \; \frac{2I^2}{m^2} \; \{ \frac{v_x^2 + v^2}{v^2} \; + \; \frac{3v_x^2 - v^2}{v^2} \; \cos \; 2\alpha \} \tag{A.2.4}$$

A.2.1   Integration with respect to $\overline{\eta}$ -

To perform the integration with respect to $\overline{\eta}$, we substitute the value of I from Eqns. (A.1.3), (A.1.9) and (A.1.11) in Eqn. (A.2.4) and in turn substitute this value for $\overline{\{c_x^2\}}$ in Eqn. (A.1.31). This reduces the $\overline{\eta}$ integration to the following

$$\int \gamma(\eta - A) \{ (g_1 A^2 + g_2 A^3) - (2Ag_1 + 3A^2 g_2)\eta + (g_1 + 3Ag_2)\eta^2 - g_2 \eta^3 \} e^{-\overline{\eta}^2} \; d\overline{\eta} \tag{A.2.5}$$

where

$$g_1 = -2 \; \frac{v_x^2}{v} \; \frac{\cos \alpha}{\zeta}, g_2 = \frac{1}{2\zeta^2} \; \{ \frac{v_x^2 + v^2}{v^2} \; + \; \frac{3v_x^2 - v^2}{v^2} \; \cos \; 2\alpha \} \tag{A.2.6}$$

and

$$A = v \cos \alpha + x$$

The above integral can also be written in the form

$$J^{3/2} \int_A^\infty \{ (\overline{g}_1 \overline{A}^2 + g_2 \overline{A}^3) - (2\overline{g}_1 \overline{A} + 3g_2 \overline{A}^2)\overline{\eta} + (\overline{g}_1 + 3g_2 \overline{A})\overline{\eta}^2 - g_2 \overline{\eta}^3 \} e^{-\overline{\eta}^2} \; d\overline{\eta} \tag{A.2.7}$$

where

$$\bar{g}_1 = -2\xi \frac{\bar{A}-\bar{X}}{\zeta} \; ; \; g_2 = \frac{1}{\zeta^2} \{(1-\xi) + (3\xi-1) (\frac{\bar{A}-\bar{X}}{\bar{v}})^2\}$$

$$\bar{A} = A\sqrt{J} \; ; \; \bar{v} = v\sqrt{J} \; ; \; \xi = (\frac{\bar{x}}{\bar{v}})^2 \; ; \; \bar{\eta} = \eta/\sqrt{J} \tag{A.2.8}$$

The integration of (A.2.7) gives us a function of $\bar{A}$, $\bar{g}_1$, g_2, J

$$F (\bar{A},\bar{g}_1,g_2)J^{3/2} = J^{3/2} \{\frac{\sqrt{\pi}}{4} (\bar{g}_1 + 3g_2 \bar{A} + 2\bar{g}_1\bar{A}^2 + 2g_2\bar{A}^3)$$

$$- \frac{1}{2} (g_2 + \bar{g}_1 \bar{A} + g_2 \bar{A}^2) e^{-\bar{A}^2} - \frac{1}{2}(\bar{g}_1 + 3g_2 \bar{A} + \bar{g}_1 \bar{A}^2$$

$$+ g_2 \bar{A}^3) \text{ erf } \bar{A}\} \tag{A.2.9}$$

A.2.2   <u>Integration with respect to</u> α :

We have from Eqns. (A.2.6) and (A.2.8)

$$\bar{A} = \bar{v} \cos \alpha + \bar{X} \tag{A.2.10}$$

This transformation is used to change the α integration to integration with respect to $\bar{A}$.   In such a case we have

$$\sin \alpha \, d\alpha = -d\bar{A}/\bar{v}$$

$$v_2 = \bar{X} + \bar{v} \text{ and } v_1 = \bar{X} - \bar{v} \tag{A.2.11}$$

where v_2 and v_1 are the lower and upper limits (corresponding to $\alpha = 0$ and $\alpha = \pi$) for the new variable A, of integration.

This means the following integral has to be evaluated

$$\frac{-J^{3/2}}{\bar{v}} \int F (\bar{A} ; \bar{g}_1, g_2) \, d\bar{A}$$

It should be noted at this stage that $\bar{g}_1$ and g_2 appearing in F , themselves are functions of $\bar{A}$, given by Eqns. (A.2.8). Thus after substituting for $\bar{g}_1$ and g_2 we get the above integral as

$$\frac{J^{3/2}}{\overline{v}} \int_{v_1}^{v_2} [\sum_{\ell=1}^{5} \{P_\ell - Q_\ell \ e^{-\overline{A}^2} - R_\ell \ \mathrm{erf} \ \overline{A}\} \ \overline{A}^\ell \ d\overline{A}$$

$$= \frac{J^{3/2}}{\overline{v}} \{H(v_2;\overline{v},\xi,\zeta,\overline{X}) - H(v_1;\overline{v},\xi,\zeta,\overline{X})\}. \qquad (A.2.12)$$

where

$$P_o = \frac{\sqrt{\pi}}{2} \ \frac{\overline{X}\xi}{\zeta} \ ; \quad P_1 = \frac{3}{2\zeta^2} \ \{\frac{3\xi-1}{\overline{v}^2} \ \overline{X}^2 + 1-\xi\}$$

$$P_2 = \frac{2\xi\overline{X}}{\zeta} - \frac{3X(3\xi-1)}{\overline{v}^2 \ \zeta^2} \ ; \quad P_3 = \frac{3(3\xi-1)}{2} \ \frac{2}{2 \ \overline{v}^2} - \frac{2\xi}{\zeta} + \frac{1-\xi}{\zeta^2} + \frac{(3\xi-1)\overline{X}^2}{\overline{v}^2 \ \zeta^2}$$

$$P_4 = - \ \frac{2(3\xi-1)\overline{X}}{\zeta^2 \ \overline{v}^2} \ ; \quad P_5 = \frac{3\xi - 1}{\zeta^2 \ \overline{v}^2}$$

$$Q_o = \frac{1-\xi}{2\zeta^2} + \frac{(3\xi-1)\overline{X}^2}{2\overline{v}^2 \ \zeta^2} \ ; \quad Q_1 = \frac{\xi \ \overline{X}}{\zeta} - \frac{X(3\xi-1)}{\zeta^2 \ \overline{v}^2}$$

$$Q_2 = \frac{3\xi - 1}{2\zeta^2 \ \overline{v}^2} - \frac{\xi}{\zeta} + \frac{1-\xi}{2\zeta^2} + \frac{(3\xi-1)\overline{X}^2}{2\zeta^2 \ \overline{v}^2} \qquad (A.2.13)$$

$$Q_3 = - \ \frac{3\xi-1}{\zeta^2 \ \overline{v}^2} \ ; \quad Q_4 = \frac{3\xi - 1}{2\zeta^2 \ \overline{v}^2}$$

$$Q_5 = 0$$

$$R_o = \frac{\xi-\overline{X}}{\zeta} \ ; \quad R_1 = \frac{3(3\xi-1)\overline{X}^2}{2\zeta^2 \ \overline{v}^2} + \frac{3(1-\xi)}{2\zeta^2} - \frac{\xi}{\zeta}$$

$$R_2 = \frac{2\xi \cdot \overline{X}}{\zeta} - \frac{3(3\xi-1)\overline{X}}{\zeta^2 \ \overline{v}^2}$$

$$R_3 = \frac{3(3\xi-1)}{2\zeta^2 \ \overline{v}^2} - \frac{2\xi}{\zeta} + \frac{1-\xi}{\zeta^2} + \frac{3\xi-1}{\zeta^2\overline{v}^2} \ \overline{X}^2$$

$$R_4 = - \ \frac{2(3\xi-1)\overline{X}}{\zeta^2 \ \overline{v}^2} \ , \quad R_5 = \frac{3\xi - 1}{\xi^2\overline{v}^2}$$

and

$$H_p = H(v_p, \overline{v}, \xi, \varsigma, \overline{X}) = \sum_{\ell=1}^{5} \{ \frac{P_\ell \ v_p^{\ell+1}}{\ell+1} - \Omega_\ell \ \Lambda_\ell(v_p) - R_\ell \textcircled{H}_\ell (v_p) \} \tag{A.2.14}$$

The integrals

$$\Lambda_n(x) = \int_0^X x^n \ e^{-x^2} \ dx \ \text{ and } \ \textcircled{H}_n(x) = \int_0^X x^n \ \text{erf} \ x \ dx \tag{A.2.15}$$

appearing in (A.2.14) have been listed in Appendix B

Integrations in the $\underset{\sim}{G}$ space :

Eqns. (A.1.11) and (A.1.20) give the following transformation for $\underset{\sim}{G}$

$$\underset{\sim}{v} = \underset{\sim}{G} - u_{ij} \ \underset{\sim}{i} \tag{A.2.16}$$

where

$$u_{ij} = u_i - u_j \tag{A.2.17}$$

Representing $\underset{\sim}{G}$ in spherical co-ordinates we have for the elemental volume in $\underset{\sim}{G}$ space as

$$d\underset{\sim}{G} = G^2 \ \sin \gamma_1 \ d\gamma_1 \ d\psi_1 \ dG \tag{A.2.18}$$

From Eqn. (A.2.16) we can get the following results easily

$$\overline{v}^2 = \overline{G}^2 - 2\overline{G} \ \overline{u}_{ij} \ \cos \gamma_1 + \overline{u}_{ij}^2$$

$$\overline{v}_x = \overline{G} \ \cos \gamma - \overline{u}_{ij} \tag{A.2.19}$$

The first of these two, gives a transformation for integrating with respect to γ_1 as

$$\sin \gamma_1 d\gamma_1 = \frac{\bar{v}\, d\, \bar{v}}{\bar{G}\, \bar{u}_{ij}} \quad . \tag{A.2.20}$$

where $\bar{G} = G/\sqrt{J}$ and $\bar{u}_{ij} = u_{ij}/\sqrt{J}$ $\qquad$ (A.2.21)

Further the Eqns. (A.2.8) and (A.2.19) give ξ as the following function of $\bar{G}$, and $\bar{u}_{ij}$

$$\xi = \left(\frac{\bar{G}^2 - \bar{v}^2 - u_{ij}^2}{2\, \bar{v}\, \bar{u}_{ij}} \right)^2 \tag{A.2.22}$$

Thus the volume element $d\, \underset{\sim}{G}$ given by Eqn. (A.2.18) reduce to

$$d\underset{\sim}{G} = J^{3/2}\, \bar{G}\, \frac{\bar{v}\, d\, \bar{v}}{\bar{u}_{ij}}\, d\bar{G}\, d\psi_1 \tag{A.2.23}$$

and the *region of integration* is

$\psi_1 : 0$ to 2π

$\bar{v} : (\bar{G} - \bar{u}_{ij})$ to $(\bar{G} + \bar{u}_{ij})$

$\bar{G} : 0$ to ∞ .

The integration with respect to ψ_1 gives a factor of 2π and the region of integration (CBDE) in the $\bar{G}$, space is shown in Fig. A.2.1. Thus we have to evaluate the *following integral*

$$\int_0^\infty dG \int_{\bar{G}-\bar{u}_{ij}}^{\bar{G}+\bar{u}_{ij}} (H_2 - H_1)\bar{G}\, e^{-\alpha\bar{G}^2}\, d\bar{v} \tag{A.2.24}$$

where

$$\overline{\alpha} = m \ J/2k(T_{t_i} + T_{t_j})$$

$$H_2 = H_2 \ (\overline{v},\overline{G};\zeta,\overline{X}) = H(v_2 \ ; \ \overline{v},\xi,\zeta,\overline{X})$$

$$H_1 = H_1 \ (\overline{v},\overline{G};\zeta,\overline{X}) = H(v_1;\overline{v},\xi,\zeta,\overline{X})$$

(A.2.25)

It can be seen from Eqn. (A.2.11), (A.2.13), (A.2.22) and (A.2.25) that

$$H_2(-\overline{v},-\overline{G};\zeta,\overline{X}) = H_2(-\overline{v},\overline{G};\zeta,\overline{X}) = H_1(\overline{v},-\overline{G};\zeta,\overline{X}) = H_1(\overline{v},\overline{G};\zeta,\overline{X})$$

(A.2.26)

The integral (A.2.24) is equivalent to the difference of the contributions due to the region ADE (Sector of circle with infinite radius and centre D, bounded by the lines $\overline{G} = 0$ and $\overline{v} = \overline{G} - \overline{u}_{ij}$) and the region ABC (sector of circle with infinite radius and centre B, bounded by lines $\overline{G} = 0$ and $\overline{v} = \overline{G} + \overline{u}_{ij}$). This is possible only when the integrand is well behaved in the domain ADE (which contains ABC as a sub domain in it), such that the integral with ∞ limit is not an improper integral. By careful study of the integrand in (A 2.24), that is, the functions given by Eqn. (A.2.13), it can be seen that the integrand is bounded due to the exponential damping terms and hence it is well behaved, in the domain ADE.

Thus we can write the integral (A.2.24) as

$$\int_{-\overline{u}_{ij}}^{\infty} d\overline{G} \int_{0}^{\overline{G}-\overline{u}_{ij}} (H_2-H_1)\overline{G}e^{-\overline{\alpha G}^2} \ d\overline{v} - \int_{\overline{u}_{ij}}^{\infty} d\overline{G} \int_{0}^{\overline{G}+\overline{u}_{ij}} (H_2-H_1)\overline{G}e^{-\overline{\alpha G}^2} d\overline{v}$$

Finally, by effecting the change of order of integrations and using the symmetric properties (A.2.26) we get the integral

$$\int_{-\infty}^{\infty} d\overline{v} \int_{\overline{v}-u_{ij}}^{\overline{v}+\overline{u}_{ij}} H_2 \ \overline{G}e^{-\overline{\alpha}\overline{G}^2} \ d\overline{G} \qquad (A.2.27)$$

where

$$H_2 = H(v_2;\overline{v},\xi,\zeta,\overline{X}) = \sum_{\ell=1}^{5} \{\frac{P_\ell \ v_2^{\ell+1}}{\ell+1} - Q_\ell \ \Lambda_\ell(v_2) - R_\ell \ \textcircled{H}_\ell(v_2)\}$$

P_ℓ, Q_ℓ, R_ℓ are functions of $\overline{v}$, ξ, ζ, $\overline{X}$ and ξ is a function of $\overline{G}, \overline{v}$, given respectively by Eqns. (A.2.13) and (A.2.22). The integration with respect $\overline{G}$ can be carried out, as H_2 is an integrable function of $\overline{G}$, through the functions P_ℓ, Q_ℓ, R_ℓ which are in turn dependent on ξ. However the analytical integration, with respect to $\overline{v}$ has been not possible. Thus we get an integral with respect to $\overline{v}$ as

$$\int_{-\infty}^{\infty} \overline{H}_2 \ (\overline{v}; \ \overline{\alpha},\zeta,\overline{X}) \ d\overline{v} \qquad (A.2.28)$$

where

$$\overline{H}_2(\overline{v},\overline{\alpha},\xi,\overline{X}) = \sum_{\ell=1}^{5} \frac{\overline{P}_\ell \ v_2^{\ell+1}}{\ell+1} - \overline{C}_\ell \ \Lambda_\ell(v_2) - \overline{R}_\ell \ \textcircled{H}_\ell(v_2) \qquad (A.2.29)$$

where

$$\overline{P}_\ell(\overline{v},\overline{\alpha},\zeta,\overline{X}) = \int_{G_1}^{G_2} P_\ell \ \overline{G} \ e^{-\overline{\alpha}\overline{G}^2} \ d\overline{G}$$

$$\overline{Q}_\ell(\overline{v},\overline{\alpha},\zeta,\overline{X}) = \int_{G_1}^{G_2} Q_\ell \ \overline{G} \ e^{-\overline{\alpha}\overline{G}^2} \ d\overline{G} \qquad (A.2.30)$$

$$\overline{R}_\ell(\overline{v},\alpha,\zeta,\overline{X}) = \int_{G_1}^{G2} R_\ell \ \overline{G} \ e^{-\overline{\alpha}G^{-2}} \ d\overline{G}$$

$$v_2 = \overline{X} + \overline{v}$$

$$C_1 = v \quad u_{11} \text{ and } C_2 \quad v + u_{11} \ .$$

The integrals (A.2.30) are listed below

$$\bar{P}_0 = \frac{\sqrt{\pi}}{2} \frac{\bar{X} \, \xi_1}{\zeta} \quad ; \qquad \bar{P}_1 = \frac{3}{2\zeta^2} \left\{ \frac{\xi_3}{\bar{v}^2} \bar{X}^2 + \xi_2 \right\}$$

$$\bar{P}_2 = \frac{3\xi_1 \, \bar{X}}{\zeta} - \frac{3\bar{X} \, \xi_3}{\bar{v}^2 \, \zeta^2} \quad ; \quad \bar{P}_3 = \frac{(3+2\bar{X})\xi_3}{2\zeta^2 \bar{v}^2} + \frac{2\xi_1}{\zeta}$$

$$\bar{P}_4 = \frac{-2\xi_3 \bar{X}}{\zeta^2 \, \bar{v}^2} \qquad ; \qquad \bar{P}_5 = \frac{\xi_3}{\zeta^2 \, \bar{v}^2}$$

$$\bar{Q}_0 = \frac{\xi_2}{2\zeta^2} + \frac{\xi_3 \, \bar{X}^2}{2\bar{v}^2 \zeta^2} \quad ; \qquad \bar{Q}_1 = \frac{\xi_1 \, \bar{X}}{\zeta} - \frac{\bar{X} \, \xi_3}{\zeta^2 \, \bar{v}^2}$$

$$\bar{Q}_2 = \frac{\xi_3 (1+\bar{X}^2)}{2\zeta^2 \, \bar{v}^2} - \frac{\xi_1}{\zeta} + \frac{\xi_2}{2\zeta^2} \quad ; \quad \bar{Q}_3 = \frac{-\xi_3}{\zeta^2 \, \bar{v}^2}$$

$$\bar{Q}_4 = \frac{\xi_3}{2\zeta^2 \bar{v}^2} \qquad ; \qquad \bar{Q}_5 = 0$$

$$\bar{R}_0 = \frac{\xi_1 \bar{X}}{\zeta} \qquad ; \qquad \bar{R}_1 = \frac{3\xi_3 \, \bar{X}^2}{2\zeta^2 \, \bar{v}^2} + \frac{2\xi_2}{2\zeta^2} - \frac{\xi_1}{\zeta}$$

$$\bar{R}_2 = \frac{2\xi_1 \, \bar{X}}{\zeta} \qquad ; \qquad \bar{R}_3 = \frac{(3+2\bar{X}^2)\xi_3}{2\zeta^2 \, \bar{v}^2} - \frac{2\xi_1}{\zeta} + \frac{\xi_2}{\zeta^2}$$

$$\bar{R}_4 = \frac{-2\xi_3 \, \bar{X}}{\zeta^2 \, \bar{v}^2} \qquad ; \qquad \bar{R}_5 \, \frac{\xi_3}{\zeta^2 \, \bar{v}^2}$$

(A.2.31)

where

$$\xi_1 = \int_{G_1}^{G_2} \xi \, \bar{G} \, e^{-\alpha \bar{G}^2} d\bar{G} = \xi_{12} - \xi_{11}$$

$$\xi_2 = \int_{G_1}^{G_2} (1-\xi) \bar{G} \, e^{-\alpha \bar{G}^2} d\bar{G} = (\xi_{02} - \xi_{01}) - (\xi_{12} - \xi_{11})$$

$$\xi_3 = \int_{G_1}^{G_2} (3\xi-1)\overline{G} \ e^{-\overline{\alpha}\overline{G}^2} d\overline{G} = 3(\xi_{12} - \xi_{11}) - (\xi_{02} - \xi_{01})$$

$$\xi_{1p} = \frac{1}{4\overline{u}_{ij}^2 \ \overline{v}^2} \ \{\frac{1}{\overline{\alpha}^3} \ \Lambda_5(G'_p) - 2(\overline{v}^2 + \overline{u}_{ij}^2) \frac{1}{\overline{\alpha}^2} \Lambda_3 \ (G'_p) + \frac{1}{\overline{\alpha}} \ \Lambda_1(G'_p) \quad (A.2.32)$$

$$\xi_{op} = \frac{1}{\overline{\alpha}} \ \Lambda_1 \ (G'_p) \ \text{ and } \ G'_p = \sqrt{\overline{\alpha}} \ G_p$$

Thus we have, the collision integral for $\overline{\phi} = c_x^2$ as a seven fold integral given by

$$I_{ij}(c_x^2) = \frac{-2n_i n_j}{\pi^4} \{\frac{m}{2k(t_{t_i}+T_{t_j})}\}^{3/2} \ (\frac{8s}{kT_{v_i}})^{1/2}(\frac{8s}{kT_{v_j}})^{1/2} \ \frac{b^2}{\overline{u}_{ij}} \int J^3$$

$$\overline{H}_2 \ (v;\overline{\alpha},\overline{\zeta},\overline{X}) \ \exp \ \{- \frac{s(2B)^2}{2kT_{v_i}} - \frac{s(2B1)^2}{2kT_{v_j}}\}\overline{K} \ d\overline{v} \ d\overline{\tau}_6 \qquad (A.2.33)$$

This expression $I_{ij} (c_x^2)$ takes o/o form when $i = j$. However it is more convinient to carry out the integration in $\underset{\sim}{G}$ space, separately for this case ($i = j$) .

From Eqn. (A.2.16), (A.2.19) and (A.2.22) we have for $i = j$

$$\overline{u}_{ij} = 0 \ ; \ \underset{\sim}{v} = \underset{\sim}{G} \ ; \ \overline{v}_x = \overline{G} \cos \gamma_1$$

$$\xi = (\frac{\overline{v}_x}{\overline{v}})^2 = \cos^2 \gamma_1. \qquad (A.2.33)$$

Thus in Eqn. (A.2.12) the functions P_ℓ, Q_ℓ, R_ℓ which are dependent on ξ can be integrated with respect to γ_1 to obtain

$$\overline{\overline{P}}_\ell \ (\overline{v},\overline{X},\zeta) = \int_0^\pi P_\ell \sin \gamma_1 \ d\gamma_1$$

$$\overline{\overline{Q}}_\ell \ (\overline{v},\overline{X},\zeta) = \int_0^\pi Q_\ell \ \sin \gamma_1 \ d\gamma_1 \qquad (A.2.34)$$

$$\overline{\overline{R}}_\ell \ (\overline{v},X,\zeta) \quad \int_0^\pi R_\ell \ \sin \gamma_1 \ d\gamma_1$$

so that the collision integral can be written as

$$I_{ii}(c_x^2) = \frac{-2n_i^2}{\pi^4} \left(\frac{m}{4kT_{t_i}}\right)^{3/2} \left(\frac{8s}{kT_{v_i}}\right) b^2 \int J^{5/2}$$

$$\overline{\overline{F}}_2(\overline{v},\overline{\alpha},\varsigma,\overline{X})\ \overline{v}\ \exp\ \{-\overline{\alpha}\ \overline{v}^2 - \frac{s(2B)^2 + s(2B_1)^2}{2k\ T_{v_i}}\}\ \overline{K}\ d\overline{v}\ d\overline{\tau}_6 \qquad (A.2.35)$$

where

$$\overline{\overline{H}}_2\ (\overline{v},\overline{\alpha},\varsigma,\overline{X})\ \sum_{\ell=1}^{5}\ \frac{\overline{\overline{P}}_\ell\ v_2^{\ell+1}}{\ell+1}\ -\ \overline{\overline{Q}}_\ell\ \Lambda_\ell(v_2) - \overline{\overline{R}}_\ell\bigodot_\ell (V_2) \qquad (A.2.36)$$

$\overline{\overline{P}}_\ell$, $\overline{\overline{Q}}_\ell$, $\overline{\overline{R}}_\ell$ are the functions $\overline{P}_\ell$, $\overline{Q}_\ell$, $\overline{R}_\ell$ given by $(A.2.31)$

in which ξ_1, ξ_2 and ξ_3 are replaced by $\overline{\xi}_1$, $\overline{\xi}_2$ and $\overline{\xi}_3$ respectively

where

$$\overline{\xi}_1 = \int_0^\pi \xi\ \sin\gamma_1\ d\gamma_1 = 2/3$$

$$\overline{\xi}_2 = \int_0^\pi (1-\xi)\ \sin\gamma_1\ d\gamma_1 = 4/3 \qquad\qquad (A.2.37)$$

$$\overline{\xi}_3 = \int_0^\pi (3\xi-1)\ \sin\gamma_1\ d\gamma_1 = 0\ .$$

Thus the collision integral for $\phi = c_x^2$ is reduced to a seven fold

integral both for the cases $i \neq j$ and $i = j$.

A.3 $\phi = 1/2\ J_1\ \omega_+^2$

$$\{\phi\} = \frac{1}{2J_1}\ I^2\ \{(b+B\cos\phi)^2\ (1-(\underset{\sim}{e}\cdot\underset{\sim}{n})^2) + (b+B_1\cos\phi_1)^2$$

$$(1-(\underset{\sim}{e}_1\cdot\underset{\sim}{n})^2)\} + I\ \{(b+B_1\cos\phi_1)\ \omega_1\cdot\underset{\sim}{e}\times\underset{\sim}{n} \qquad (A.3.1)$$

$$-\ (b+B\cos\phi)\underset{\sim}{\omega}\cdot\underset{\sim}{c}_1\times\underset{\sim}{n}\}$$

Further using the transformation for $\underset{\sim}{e}$, $\underset{\sim}{n}$, $\underset{\sim}{\omega}$ and $\underset{\sim}{\omega}_1$ we can rewrite this as

$$\{\underset{\sim}{\Phi}\} = \frac{1}{2}\frac{I^2}{J_1}[(b+B_1 \cos \phi_1)^2 \sin^2\beta_1 + (b+B \cos \phi)^2 \sin^2\beta] - I\eta \qquad (A.3.2)$$

where I, η, β, β_1 are given by Eqns. $(A.1.3)$, $(A.1.8)$, $(A.1.9)$, $(A.1.10)$, $(A.1.28)$ and $(A.1.32)$. In this case $\{\underset{\sim}{\Phi}\}$ is independent of δ , so

$$\int_0^{2\pi} \{\underset{\sim}{\Phi}\} \, d\delta = 2\pi \, \overline{\{\underset{\sim}{\Phi}\}} \; ; \qquad \overline{\{\underset{\sim}{\Phi}\}} = \{ \underset{\sim}{\Phi} \}$$

Integration with respect to $\bar{\eta}$

Substituting this $\overline{\{\underset{\sim}{\Phi}\}}$ in Eqn. $(A.1.31)$ we find that the following integral in $\bar{\eta}$ appears in $I_{ij}(\underset{\sim}{\Phi})$.

$$J^{3/2} \int \gamma(\bar{\eta}-\bar{A}) \; \{\mu_1 (\bar{A}-\bar{\eta})^3 + \mu_2 \, \bar{\eta} \, (\bar{A}-\bar{\eta})^2\} \, e^{-\bar{\eta}^2} \, d\bar{\eta} \qquad (A.3.3)$$

where

$$\mu_1 = \frac{m^2}{2\zeta^2 J_1} \; \{(b+B_1 \cos \phi_1)^2 \sin^2 \beta_1 + (b + B \cos \phi)^2 \sin^2 \beta\}$$

$$\mu_2 = \frac{m}{\zeta} \qquad \text{and} \qquad\qquad (A.3.4)$$

A is given by Eqn. $(A.2.6)$

The integral $(A.3.3)$ can be rewritten with the proper limits for $\bar{\eta}$ and after carrying out the $\bar{\eta}$ integration we get the form

$$J^3 \int_A^\infty \{\mu_1 \bar{A}^3 + (\mu_2 - 3\mu_1) \, \bar{A}^2 \, \bar{\eta} + (3\mu_1 - 2\mu_2) \, \bar{A} \, \bar{\eta}^2 + (\mu_2 - \mu_1) \, \bar{\eta}^3\} \, e^{-\bar{\eta}^2} \, d\bar{\eta}$$

$$= J^{3/2} \, \{\frac{\sqrt{\pi}}{4} \, [(3\mu_1 - 2\mu_2)\bar{A} + 2\mu_1 A^3] + \frac{1}{2} \, (\mu_2 - \mu_1) - \mu_1 \, \bar{A}^2]$$

$$\ldots e^{-\overline{A}^2} + \frac{1}{2} \left[(3\mu_1 - 2\mu_2)\overline{A} + \mu_1 \overline{A}^3 \right] \text{erf } \overline{A} \}$$

$$= J^{3/2} \mathcal{F}_1 (\overline{A} ; \mu_1, \mu_2) .$$

Integration with respect to α

The same transformation used for the earlier case, given by Eqn. (A.2.11) is adopted for the α integration, to obtain the integral as

$$\frac{J^{3/2}}{\overline{v}} \int_{v_1}^{v_2} \mathcal{F}_1(\overline{A};\mu_1,\mu_2)d\overline{A} = \frac{J^{3/2}}{\overline{v}} \{S(v_2;\mu_1,\mu_2) - S(v_1;\mu_1,\mu_2)\} \qquad (A.3.6)$$

where

$$S_p = S(v_p ; \mu_1, \mu_2) = \{ \frac{\sqrt{\pi}}{8} \left[(3\mu_1 - 2\mu_2) v_p^2 + \mu_1 v_p^4 \right] +$$

$$+ \frac{1}{16} \left[4\mu_2 - 3\mu_1) - 4(3\mu_1 - 2\mu_2) v_p^2 - 4\mu_1 v_p^4 \right] \text{erf } v_p + \frac{1}{16} \left[(4\mu_2 - 5\mu_1)v_p \right.$$
$$\left. - \frac{\mu_1}{8} v_p^3 \right] e^{-v_p^2} \qquad (A.3.7)$$

Integration in $\underset{\sim}{G}$ space :

Here again the integrations are done by adopting the transformations used in the earlier case given by Eqns. (A.2.18) and (A.2.23). Thus we have to find the integral

$$\frac{J^{7/2}}{\overline{u}_{ij}} \int_0^\infty d\overline{G} \int_{\overline{G}-\overline{u}_{ij}}^{\overline{G}+\overline{u}_{ij}} (S_2 - S_1) \overline{G} e^{-\overline{\alpha}\overline{G}^2} d\overline{v} \qquad (A.3.8)$$

Both these integrations can be done analytically, with out effecting the change of order of integrations, unlike in the case of $\zeta = C_x^2$

Integrating with respect to $\overline{v}$ we get from (A.3.8)

$$\frac{J^{7/2}}{\overline{u}_{ij}} \int_0^\infty (\overline{S}_1 - \overline{S}_2 + \overline{S}_3 - \overline{S}_4) \ \overline{G} \ e^{-\overline{\overline{G}}^2} \ d\overline{G} \tag{A.3.9}$$

where

$$\overline{S}_p = \overline{S}(\overline{G}_p \ ; \ \mu_1, \mu_2) = \{\frac{\sqrt{\pi}}{120} \ [5(3\mu_1 - 2\mu_2)\overline{G}_p^3 + 3\mu_1 \ \overline{G}_p^5]$$

$$+ \frac{1}{240} \ [15 \ (4\mu_2 - 3\mu_1)\overline{G}_p - 20 \ (3\mu_1 - 2\mu_2)\overline{G}_p^3 - 12\mu \ \overline{G}_p^5] \tag{A.3.10}$$

$$\mathrm{erf} \ \overline{G}_p + \frac{1}{480} \ [(40\mu_2 - 24\mu_1) + (40\mu_2 - 54\mu_1)\overline{G}_p^2 - 12\mu_1 \ \overline{G}_p^4] \ e^{-\overline{G}_p^2}\}$$

$$\overline{G}_1 = \overline{G} + X_1 \ ; \ \overline{G}_2 = \overline{G} + X_2$$

$$\overline{G}_3 = -\overline{G} + X_2; \ \overline{G}_4 = -\overline{G} + X_1. \tag{A.3.11}$$

Integration with respect to $\overline{G}$ is carried out using the transformations (A.3.11) and after rearranging the terms we get from (A.3.9) the required integral as

$$\frac{J^{7/2}}{\overline{u}_{ij}} \ \{\overline{\overline{S}}(X_1;\overline{a},\zeta) - \overline{\overline{S}} \ (X_2 \ ; \ \overline{a},\zeta)\} \tag{A.3.12}$$

where

$$\overline{\overline{S}}_p = \overline{\overline{S}}(X_p \ ; \ \overline{a},\zeta) = \frac{n}{\zeta^2} \ \{\frac{\sqrt{\pi}}{120} \ [5(\zeta-3)\{\chi_4(\overline{a},X_p)$$

$$- X_1 \ \chi_3(\overline{a},X_p)\} + 3(\zeta-1) \ \{\chi_6(\overline{a},X_p) - X_p \ \chi(\overline{a},X_p)\}]$$

$$+ \frac{1}{240} \ [15 \ (\zeta+5) \ \{\psi_2(\overline{a},X_p) - X_p \ \psi_1(\overline{a},X_p)\}$$

$$+ 20(\zeta- 3) \ \{X_p \ \psi_3(\overline{a},X_p) - \psi_4(\overline{a},X_p)\} +$$

$$12(\zeta-1) \ \{X_n \ \psi_5 \ (a,X_p) \quad \psi_6(a,X_p)\}] + \frac{1}{240} \ [$$

$$4(2\zeta+3) \ \{Z_1(\overline{\alpha},X_p) - X_p \ Z_0(\overline{\alpha},X_p) \ - \ (27-7\zeta)$$

$$\{X_p \ Z_2(\overline{\alpha},X_p) - Z_3(\overline{\alpha},X_p)\} + 6(\zeta-1)\{X_p Z_4(\overline{\alpha},X_p) - Z_5(\overline{\alpha}-X_p)\}]\}$$

The integrals

$$X_n(\alpha,x) = \int_{-\infty}^{\infty} e^{-\alpha(G-x)^2} \ G^n \ dG$$

$$\Psi_n(\alpha,x) = \int_{-\infty}^{\infty} e^{-\alpha(G-x)^2} \ G^n \ e^{-G^2} \ dG \tag{A.3.14}$$

and

$$Z(\alpha,x) = \int_{-\infty}^{\infty} e^{-\alpha(G-x)^2} \ G^n \ \text{erf} \ G \ dG$$

have been evaluated and given in Appendix B.

Further before arriving at $(A.3.12)$, the quantities μ_1 and μ_2 appearing in $(A.3.10)$ are expressed in terms of ζ using Eqns. $(A.1.10)$ and $(A.3.4)$. Using the result $(A.3.12)$ in Eqn. $(A.1.31)$ we get the collision integral for this case as

$$I_{ij} \ (\tfrac{1}{2} J_1 \ w^2) = \frac{-2r_i \ n_j}{s^4} \ \{\frac{m}{2k(T_{t_i}+T_{t_j})}\}^{3/2} \ \{\frac{8s}{kT_{v_i}}\}^{1/2} \ \{\frac{8s}{kT_{v_j}}\}^{1/2} \ \frac{b^2}{\overline{u}_{ij}}$$

$$\int J^{7/2} \ (\overline{\overline{S}}_1 - \overline{\overline{\Sigma}}_2) \ \exp \ \{ - \frac{s(2B)^2}{2kT_{v_i}} - \frac{s(2\Gamma_1)^2}{2k \ T_{v_j}}\} \ d\overline{\tau}_6 \tag{A.3.15}$$

This is a six fold integral which has to be evaluated numerically. As in the c_x^2 case, when $i = j$, this reduces to a o/o form. To obtain the collision integrals for such a case we follow the same as followed for the c_x^2 case.

As the integrand is independent of γ_1, the integration with respect to γ_1 give a factor

$$\int_0^\pi \sin \gamma_1 \, d\gamma_1 = 2.$$

Thus we get the collision integral

$$I_{ii}\left(\tfrac{1}{2} J_1 a_\perp^2\right) = \frac{-4n_\perp^2}{\pi^4} \left(\frac{\pi}{4kT_{t_i}}\right)^{3/2} \left(\frac{8s}{kT_{v_i}}\right) b^2 \int_{-\infty}^\infty J^2 \, S(v_2, \mu_1, \mu_2)$$

$$\bar{v} \exp\left\{-\bar{a}\bar{v}^2 - \frac{s(2B)^2 + s(2B_1)^2}{2k \, T_{v_i}}\right\} \, \bar{K} \, d\bar{v} \, d\bar{\tau}_6$$

which is obviously a seven fold integral. It has not been possible to carryout the $\bar{v}$ integration analytically for $i = j$ case.

A.4 $\bar{\xi} = 1/2 \, s(2B)^2$:

Using Eqns. (A.1.5) we can obtain for this case

$$\{\bar{\xi}\} = - \, I \, v \, (B_1 \sin \phi_1 \cos \beta_1 - B \sin \phi \cos \beta) \qquad (A.4.1)$$

As this is independent of ϵ in this case we get

$$\overline{\{\bar{\phi}\}} = \{\bar{\phi}\}$$

Integration with respect to $\bar{n}$:

Substituting for I from Eqn. (A.1.8),(A.1.9), (A.1.10),(A.1.28) and (A.1.32) we get the following integral in $\bar{n}$

$$J \int_A^\infty \bar{v} \, (\bar{A}-\bar{n})^2 \, e^{-\bar{n}^2} \, d\bar{n} \qquad (A.4.2)$$

where $\bar{v} = \dfrac{vm}{\zeta} \, (B \sin \phi \cos \beta - B_1 \sin \phi \cos \beta)$

$$= + \frac{vm}{\zeta} \, X$$

$$(A.4.3)$$

Integrating $(A.4.2)$ we get

$$\bar{v}\ \phi_2(\bar{A}) = \bar{v}\ \{\frac{\sqrt{\pi}}{4}\ (1+2\bar{A}^2) - \frac{1}{2}\ (1+2\bar{A}^2)\ \text{erf}\ \bar{A} - \frac{1}{2}\ \bar{A}e^{-\bar{A}^2}\}\quad (A.4.4)$$

Integration with respect to α:

This is done by using new variable $\bar{A}$, as indicated earlier. After the $\bar{A}$ integration we get

$$\frac{J\bar{v}}{\bar{v}}\cdot\int_{v_1}^{v_2}\phi_2(\bar{A})\,d\bar{A} = \frac{J\bar{v}}{\bar{v}}\ \{V(v_2) - V(v_1)\}\quad\quad (A.4.5)$$

where

$$V_p = V(v_p) = \{\frac{\sqrt{\pi}}{12}\ (3v_p + 2v_p^3) - \frac{1}{6}\ (1 + v_p^2)\ e^{-v_p^2}\ -$$

$$\frac{1}{6}\ (3v_p + 2v_p^3)\ \text{erf}\ v_p\}\quad\quad (A.4.6)$$

Integration in $\underset{\sim}{G}$ space :

Here again the procedure used in the earlier case is adopted to obtain the required integral as

$$\frac{J^{5/2}\ \bar{v}}{\bar{u}_{ij}}\int_0^\infty d\bar{G}\int_{\bar{G}-\bar{u}_{ij}}^{\bar{G}+\bar{u}_{ij}}(V_2 - V_1)\ \bar{G}\ e^{-\alpha\bar{G}}\ d\bar{v}\quad\quad (A.4.7)$$

Integration with respect $\bar{v}$ gives us the above integral as

$$\frac{J^{5/2}\ \bar{v}}{\bar{u}_{ij}}\int_0^\infty (\bar{V}_1 - \bar{V}_2 + \bar{V}_3 - \bar{V}_4)\bar{G}\ e^{-\alpha\bar{G}^2}\ d\bar{G}\quad\quad (A.4.8)$$

where

$$V_p = \overline{V}(G_p) = \{\frac{\sqrt{\pi}}{24} (3G_r^2 - G_p^4) - \frac{1}{48} (5G_p +$$

$$2G_p^3) \ e^{-G_p^2} - \frac{1}{48} (3 + 12G_p^2 + 4G_p^4) \ \text{erf} \ G_p\} \qquad (A.4.9)$$

and G_p are same as given by Eqn. $(\wedge.3.11)$.

Carrying out the $\overline{G}$ integration and rearranging terms gives the integral $(4.4.8)$ as

$$\frac{J^{5/2} \ \overline{\upsilon}}{\overline{u}_{ij}} \ \{\overline{\overline{V}}(\overline{\alpha}, X_2) - \overline{\overline{V}}(\overline{\alpha}, X_1)\} \qquad (A.4.10)$$

where

$$\overline{\overline{V}}_p = \overline{\overline{V}}(\overline{\alpha}, X_p) = \{\frac{\sqrt{\pi}}{24} [\{X_3(\overline{\alpha}, X_p) - 3X_p \ X_2(\overline{\alpha}, X_p)\}$$

$$+ \{X_5 (\overline{\alpha}, X_p) - X_p \ X_4(\overline{\alpha}, X_p)\}]$$

$$- \frac{1}{48} [5 \{\psi_2(\overline{\alpha}, X_p) - X_p \ \psi_1(\overline{\alpha}, X_p)\} + 2 \{\psi_4(\overline{\alpha}, \overline{X}_p)$$

$$-X_p \ \psi_3(\overline{\alpha}, X_p)\}] - \frac{1}{48} [3\{Z_1(\overline{\alpha}, X_p) - X_p \ Z_0(\overline{\alpha}, X_p)\}$$

$$+ 12\{Z_3(\overline{\alpha}, X_p) - X_p \ Z_2(\overline{\alpha}, X_p)\} + 4 \{Z_5(\overline{\alpha}, X_p) + X_p \ Z_4(\overline{\alpha}, X_p)\}]\}$$

Finally we can write down the collision integral for this case as

$$I_{ij} \ (\frac{s(2B)^2}{2}) = \frac{-2n_i \ n_j}{\pi^4} \{\frac{m}{2k(T_{t_i}+T_{t_j})}\}^{3/2} \ (\frac{8s}{kT_{v_i}})^{1/2} \ (\frac{8s}{kT_{v_j}})^{1/2} \ \frac{b^2}{\overline{u}_{ij}}$$

$$\int J^{5/2} \ \overline{\upsilon} \ \{\overline{\overline{V}}_2 - \overline{\overline{V}}_1\} \ \exp \ \{-\frac{s(23)^2}{2k \ T_{v_i}} - \frac{s(2B_1)^2}{2k \ T_{v_j}}\} \ d\overline{\tau}_6 \qquad (A.4.12)$$

Some of the important integrals used in Appendix A have been listed
here.

B.1 Integrals $\Lambda_n(x) = \int x^n e^{-x^2} dx$:

$\Lambda_0 = \text{erf } x$

$\Lambda_1 = -e^{-x^2}/2$

$\Lambda_2 = (\text{erf } x - x e^{-x^2})/2$

$\Lambda_3 = -\frac{1}{2}(1 + x^2) e^{-x^2}$

$\Lambda_4 = \frac{1}{4}\{3 \text{ erf } x - e^{-x^2}(3x + 2x^3)\}$

$\Lambda_5 = -\frac{1}{2}(x^4 + 2x^2 + 2) e^{-x^2}$

$\Lambda_6 = \frac{1}{8}\{15 \text{ erf } x - (15x + 10x^3 + 4x^5)e^{-x^2}\}$

B.2 Integrals $\mathbb{H}_n(x) = \int x^n \text{ erf } x \, dx$:

$\mathbb{H}_0 = x \text{ erf } x + e^{-x^2}/2$

$\mathbb{H}_1 = \frac{1}{4}\{(2x^2 - 1) \text{ erf } x + x e^{-x^2}\}$

$\mathbb{H}_2 = \frac{1}{6}\{(2x^3 \text{ erf } x + (x^2 + 1) e^{-x^2}\}$

$\mathbb{H}_3 = \{\frac{1}{16}(4x^3 - 3) \text{ erf } x + (2x^3 + 3x)e^{-x^2}\}$

$\mathbb{H}_4 = \frac{1}{10}\{2x^5 \text{ erf } x + (x^4 + 2x^2 + 2) e^{-x^2}\}$

$\mathbb{H}_5 = \frac{1}{48}\{(8x^6 - 15) \text{ erf } x + (4x^5 + 10x^3 + 15x) e^{-x^2}\}$

B.3   Integrals

$$X_n(\alpha, x) = \int_{-\infty}^{\infty} G^n \, e^{-\alpha(G-x)^2} \, dG$$

$$X_0 = \sqrt{\pi/\alpha}$$

$$X_1 = x X_0$$

$$X_2 = (1 + 2\alpha x^2) \, X_0/2\alpha$$

$$X_3 = (3 + 2\alpha x^2) \, x \, X_0/2\alpha$$

$$X_4 = (3 + 12\alpha \, x^2 + 4\alpha^2 x^4) \, X_0/4\alpha^2$$

$$X_5 = (15 + 20\alpha \, x^2 + 4\alpha^2 x^4) x \, X_0/4 \, \alpha^2$$

$$X_6 = (15 + 90\alpha \, x^2 + 60 \, \alpha^2 x^4 + 8 \, \alpha^3 x^6) \, X_0/8\alpha^3$$

B.4   Integrals $\psi_n(\alpha, x) = \int_{-\infty}^{\infty} G^n \, e^{-\alpha(G-x)^2 - G^2} \, dG$

$$\psi_0 = \sqrt{\pi/(1+\alpha)} \, \exp \{-\alpha x^2/(1+\alpha)\}$$

$$\psi_1 = \alpha x \, \psi_0/(1+\alpha)$$

$$\psi_2 = (1+\alpha+2\alpha^2 x^2) \, \psi_0/2(\alpha+1)^2$$

$$\psi_3 = \{3\alpha \, (1+\alpha) + 2\alpha^3 \, x^2\} \, x \, \psi_0/2(1+\alpha)^3$$

$$\psi_4 = \{3(\alpha+1)^2 + 12(\alpha+1)\alpha^2 \, x^2 + 4\alpha^4 \, x^4\} \, \psi_0/4 \, (\alpha+1)^4$$

$$\psi_5 = \{15\alpha(1+\alpha)^2 + 20\alpha^3 \, (1+\alpha)x^2 + 4\alpha^5 \, x^4\} \, x \, \psi_0/4(\alpha+1)^5$$

B.5 Integrals $Z(\alpha,x) = \int_{-\infty}^{\infty} G^n \text{ erf } C \; e^{-\alpha(G-x)^2} dG$

By putting $y = \sqrt{\frac{\alpha}{1+\alpha} x^2}$ following results are listed.

$Z_o = X_o \text{ erf } y$

$Z_1 = (e^{-y^2}/2\sqrt{\alpha(\alpha+1)} + x \text{ erf } y) \chi_o$

$Z_2 = \{ \frac{(1+2\alpha x^2)}{2\alpha} \text{ erf } y + \frac{(2\alpha+1) x}{2\sqrt{\alpha(1+\alpha)^3}} e^{-y^2} \} \chi_o$

$Z_3 = [\frac{(2\alpha x^2 + 3)x}{2\alpha} \text{ erf } y +$

$\frac{\{6x^2\alpha^3 + (3+6x^2)\alpha^2 + (5+2x^2)\alpha + 2\}}{4(\alpha+1)^{5/2} \alpha^{3/2}} e^{-y^2}] \chi_o$

$Z_4 = [(4\alpha^2 x^4 + 12\alpha x^2 + 3) \text{ erf } y/4\alpha^2$

$+ \{ 8x^3 + \alpha^4 + (12x^3 + 12x) \alpha^3 + (8x^3 + 26x) \alpha^2$

$+ (2x^3 + 19x) \alpha + 5x \} e^{-y^2}/ [4\alpha^{3/2}(\alpha+1)^{7/2}]] \chi_o$

$Z_5 = [\{ 4\alpha^2 x^4 + 20\alpha x^2 + 15 \} x \text{ erf } y/4\alpha^2$

$+ \{ (15\alpha^2 + 20\alpha + 8) (1+\alpha)^2 + 2x^2 (\alpha+1) \alpha$

$(30\alpha^2 + 50\alpha^2 + 35\alpha + 9) + 4x^2\alpha^2 (5\alpha^4 + 10\alpha^3 + 10\alpha^2 + 5\alpha + 1) \} e^{-y^2}] \chi_o .$

$Z_6 = (A \text{ erf } y + Be^{-y^2}) \chi_o /(\alpha+1)^3 \alpha^{7/2}$

where

$$A = \frac{15}{8} \alpha^3 + \frac{45}{4} \alpha^3 (\alpha + 1) x^2 + \frac{15}{2} \alpha^3 (\alpha + 1)^2 x^4$$

$$+ \alpha^3 (1 + \alpha)^3 x^6 + \frac{45}{8} \alpha^2 + \frac{45}{2} \alpha^2 x^2 (\alpha + 1)$$

$$+ \frac{15}{2} \alpha^2 x^4 (\alpha + 1)^2 + \frac{45}{8} \alpha + \frac{45}{4} \alpha x^2 (\alpha + 1)$$

$$+ \frac{15}{8} .$$

$$B = \{ \frac{45}{4} \alpha^2 x + 15 \alpha^2 (\alpha + 1) x^3 + 3 \alpha^2 (\alpha + 1)^2 x^5 \}$$

$$\sqrt{\alpha(\alpha + 1)} - \{ \frac{45}{8} \alpha^2 + \frac{45}{2} x^2 \alpha^2 (\alpha + 1)$$

$$+ \frac{15}{2} x^4 \alpha^2 (1 + \alpha)^2 \} y + \{ 15x \alpha + 10x^3$$

$$\alpha(\alpha + 1) \} (1 + y^2) \sqrt{\alpha(\alpha + 1)} - \{ \frac{15}{8} \alpha + \frac{15}{4} x^2$$

$$\alpha(\alpha + 1) \} (3y + 2y^3) + \{ 3x (y^4 + 2y^2 + 2)$$

$$\sqrt{\alpha(\alpha + 1)} - \frac{1}{8} (15 + 10y^2 + 4y^4) y .$$

APPENDIX C

C.1 Collision Integrals D_{ij} and D_{oij}:

From Chapter 5 we have

$$D_{ij} = \int [f_i, f_j]\, d\tau$$

$$= \int f_i f_j\, \gamma(-\underline{g}.\underline{n})\, K\, d\underline{n}\, d\tau_1\, d\tau \qquad (C.1.1)$$

Following the procedure given in Appendix A, 16 integrations were carried out for the case $i \neq j$, to get the six fold integral

$$D_{ij} = -\frac{n_i\, n_j}{4\sqrt{\pi}} \{\frac{m}{2\pi k(T_{t_i}+T_{t_j})}\}^{3/2}\ \frac{1}{u_{ij}} \int\ J^{5/2}\ \{R_s(\bar{\alpha},\overline{X}_1)-R_s(\bar{\alpha},\overline{X}_2)\}\exp\{$$

$$-\frac{s(2B)^2}{2k\, T_{v_i}} - \frac{s(2B_1)^2}{2k\, T_{v_j}}\}\ \sin\beta\ \sin\beta_1\ d\beta\ d\beta_1\ dB\ dB_1\ d\phi\ d\phi_1$$

$$(C.1.2)$$

where

$$R_s(\alpha, X) = \{\frac{\sqrt{\pi}}{2}\ (X_4 - x\ X_3)\ - \frac{1}{24}\ (-6x\ Z_1$$

$$+ 6Z_2 - 4x\ Z_3 + 4\ Z_4)\ - \frac{1}{24}\ (-2x\ \psi_0$$

$$- 2\psi_1 - 2\psi_2 + 2\psi_3) \qquad (C.1.3)$$

The quantities u_{ij}, $\bar{\alpha}$, $\overline{X}_1$, $\overline{X}_2$, and J appearing in Eqn. (C.2.2) have already been defined in Appendix A and the integrals X_n, Z_n, ψ_n are listed in Appendix B.

For $i = j$ we have

$$D_{ii} = -n_i^2 \sqrt{\pi} \{\frac{m}{4\pi k\, T_{t_i}}\}^{3/2} \int J^2$$

$$R_{sd}\ (\bar{\alpha},\bar{X})\ \exp\ \{- [\frac{s(2B)^2 + s(2B_1)^2}{2k\, T_{v_i}}]\}$$

$$\sin\beta\ \sin\beta_1\ d\beta\ d\beta_1\ dE\ dE_1\ d\phi\ d\phi_1 \qquad (C.1.4)$$

where

$$R_{sd}\ (\alpha,x) = \frac{\sqrt{\pi}}{4}\ (X_3 - x\, X_2) - \frac{1}{4}\ (Z_3 - 2x\, Z_2 + Z_1 - x Z_0) + \frac{1}{4}\ (\psi_2 - x\psi_1) \quad (C.1.5)$$

Here again all the quantities used are defined in either Appendix A or B. The collision integral D_{oi2} in the atomic species conservation equation may be obtained as a special case of D_{ij} by effecting following substitution as indicated in Chapter 2 or 3.

$$E_1 = 0,\ \phi_1 = 0,\ \varphi = 0,\ \beta_1 = 0 \qquad (C.1.6)$$

C.2 Collision Integrals $R_{ij}(\phi)$ and $R_{oi2}(\phi)$:

We can write the expression for integrals $R_{ij}(\frac{1}{2}\, s(2B)^2)$ straight-away using results of section C.1 as follows.

For $i \neq j$

$$R_{ij}\ (\frac{1}{2} s(2B)^2) = \frac{n_i\, n_j}{4\,\sqrt{\pi}}\ \{\frac{m}{2\pi k (T_{t_i} + T_{t_j})}\}^{3/2}\ \frac{1}{u_{ij}}$$

$$\int J^{5/2}\ \{R_s(\bar{\alpha},\bar{X}_1) - R_s(\bar{\alpha},\bar{X}_2)\ \{\frac{1}{2} s(2B)^2\}\ \exp\ \{- \frac{s(2B)^2}{2k\, T_{v_i}} \qquad (C.2.1)$$

$$- \frac{s(2B)^2}{2k\, T_{v_j}}\}\ \sin\beta\ \sin\beta_1\ d\beta\ d\beta_1\ dE\ dB_1\ d\phi\ d\phi_1$$

and for $i = j$

$$R_{ii} \; (\tfrac{1}{2} s(2\eta)^2) = - n_1^2 \; \sqrt{\pi} \; \{\frac{n}{4\pi k T_{t_i}}\}^{3/2} \int J^2$$

$$R_{sd} \; (\bar{a},\bar{X}) \; \{\tfrac{1}{2} s(2B)^2\} \; \exp \; \{[\frac{s(2B)^2 + s(2\beta_1)^2}{2k \; T_{v_1}}]\}$$

$$\sin \beta \sin \beta_1 \; d\beta \; d\beta_1 \; dB \; dB_1 \; d\phi \; d\phi_1 \tag{C.2.2}$$

For the integrals $R_{ij} \; (\frac{1}{2} J_1 \, \omega_\perp^2)$ the method indicated in Appendix A is followed and we can write for the final six fold integral for the case $i \neq j$ as

$$R_{ij} \; (\tfrac{1}{2} J_1 \, \omega_\perp^2) = \int [f_i, f_{ij}] \; (\tfrac{1}{2} J_1 \, \omega_\perp^2) \; d\tau$$

$$= - \frac{n_1 \, n_j}{4\sqrt{\pi}} \; \{\frac{m}{2\pi k (T_{t_i} + T_{t_j})}\}^{3/2} \; \frac{1}{u_{ij}} \int J^{3/2}$$

$$\{P_r \; (\bar{a}, \bar{X}_1) - R_r \; (\bar{a}, \bar{X}_2)\} \; \exp \; \{- \frac{s(2B)^2}{2kT_{v_1}}$$

$$- \frac{s(2B_1)^2}{2kT_{v_j}}\} \; \sin \beta \sin \beta_1 \; d\beta \; d\beta_1 \; dB \; dB_1 \; d\phi \; d\phi_1 \tag{C.2.3}$$

where

$$R_r(\bar{a}, X) = \frac{1}{8} \; \{\frac{\sqrt{\pi}}{3} \; (\chi_4 - x \, \chi_3) - [Z_3 - (3-x) \, Z_2$$

$$- (x + \tfrac{1}{2}) \, Z_1 + \tfrac{x}{2} Z_0] + [\tfrac{1}{2} \psi_0 + (1 - \tfrac{x}{2}) \, \psi_1 - x \, \psi_0]\} \tag{C.2.4}$$

For $i = j$ we have

$$\Delta \left(\frac{1}{2} J_1 \omega_1^2\right) = - n_i^2 \sqrt{\pi} \left(\frac{m}{4\pi k\, T_{t_i}}\right)^{3/2} \int J^2$$

$$rd(\overline{\sigma},x)\ \exp\ \left(- \frac{s(2E)^2 + s(2E_1)^2}{2k\, T_{V_i}}\right)\ \sin \beta \sin \beta_1$$

$$d\beta\ d\beta_1\ dB\ dB_1\ d\phi\ d\phi_1.$$

(C.2.5)

ain the integrals $E_{0i2}(\frac{1}{2})$ from $R_{ij}(\phi)$ the same substitution

ted in Eqn. (C.1.6) is used.

Thus we have all the required collision integrals for the
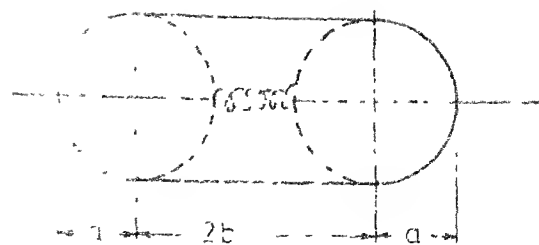
iating case.

FIG. 1. RIGID PLASTIC SPHEROCYLINDER PROJECTILE.

$r = be + an$
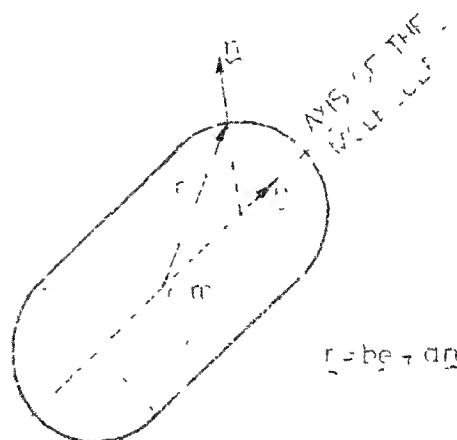
FIG. 2. SURFACE REPRESENTATION
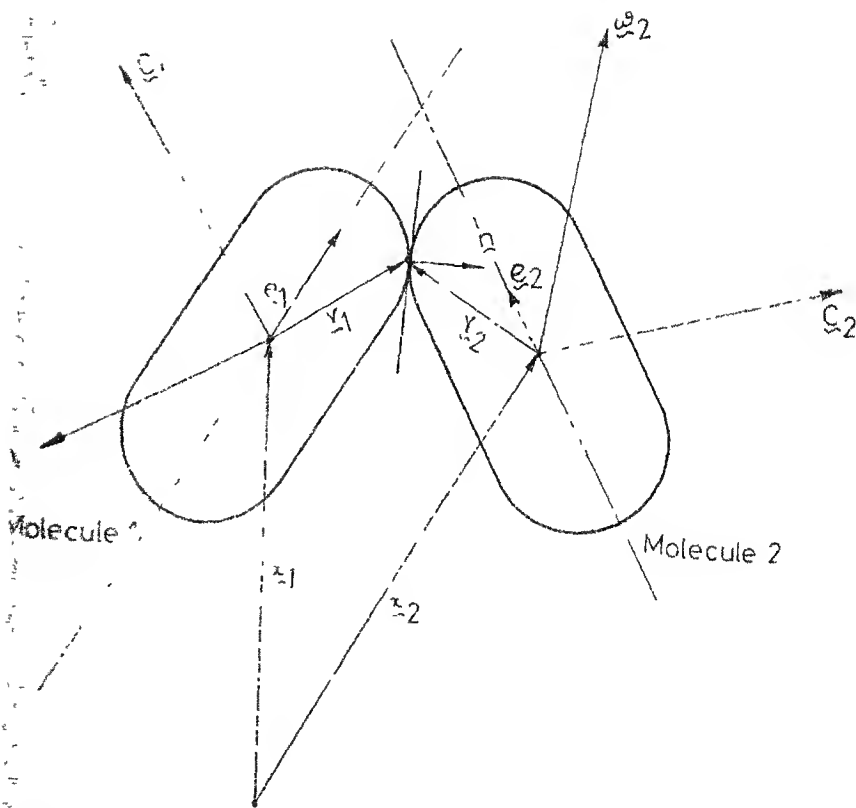
5.2 3 1_ COLLISION GEOMETRY
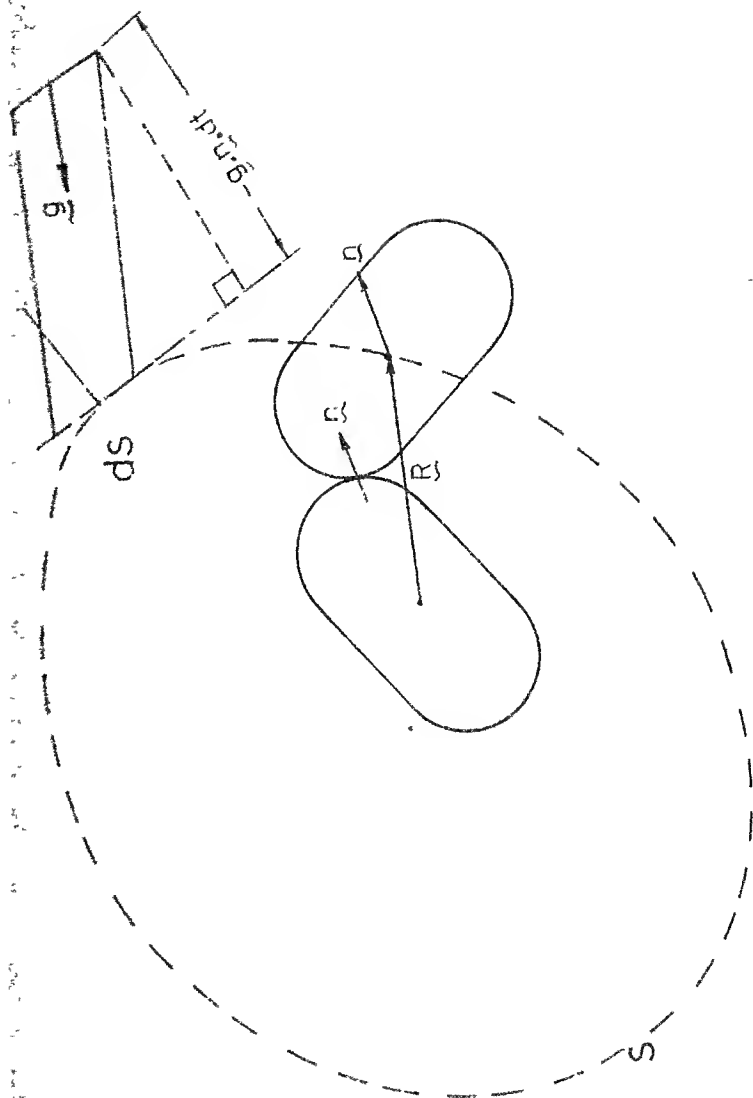
FIG 3.3.1_ INTERACTION SURFACE
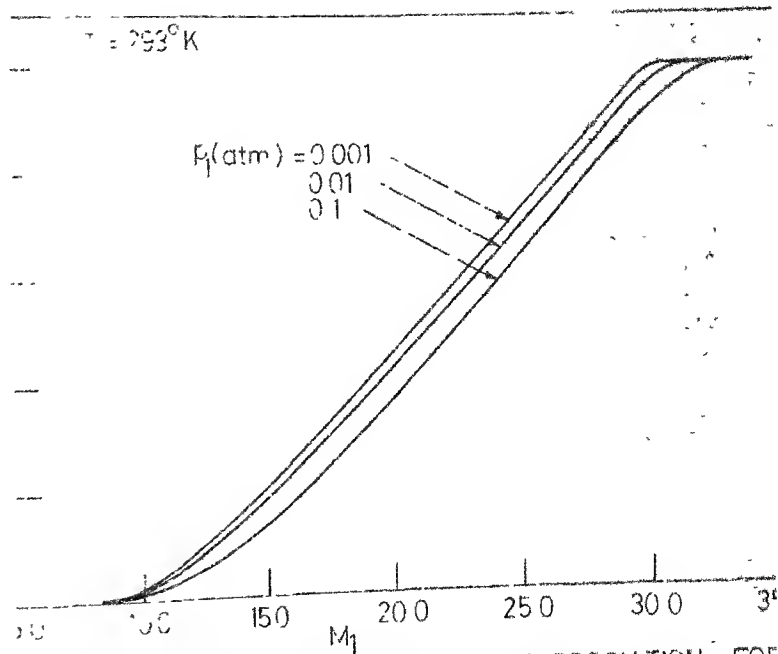
FIG 5.1.1. EQUILIBRIUM DEGREE OF DISSOCIATION FOR
NITROGEN BEHIND A NORMAL SHOCK WAVE
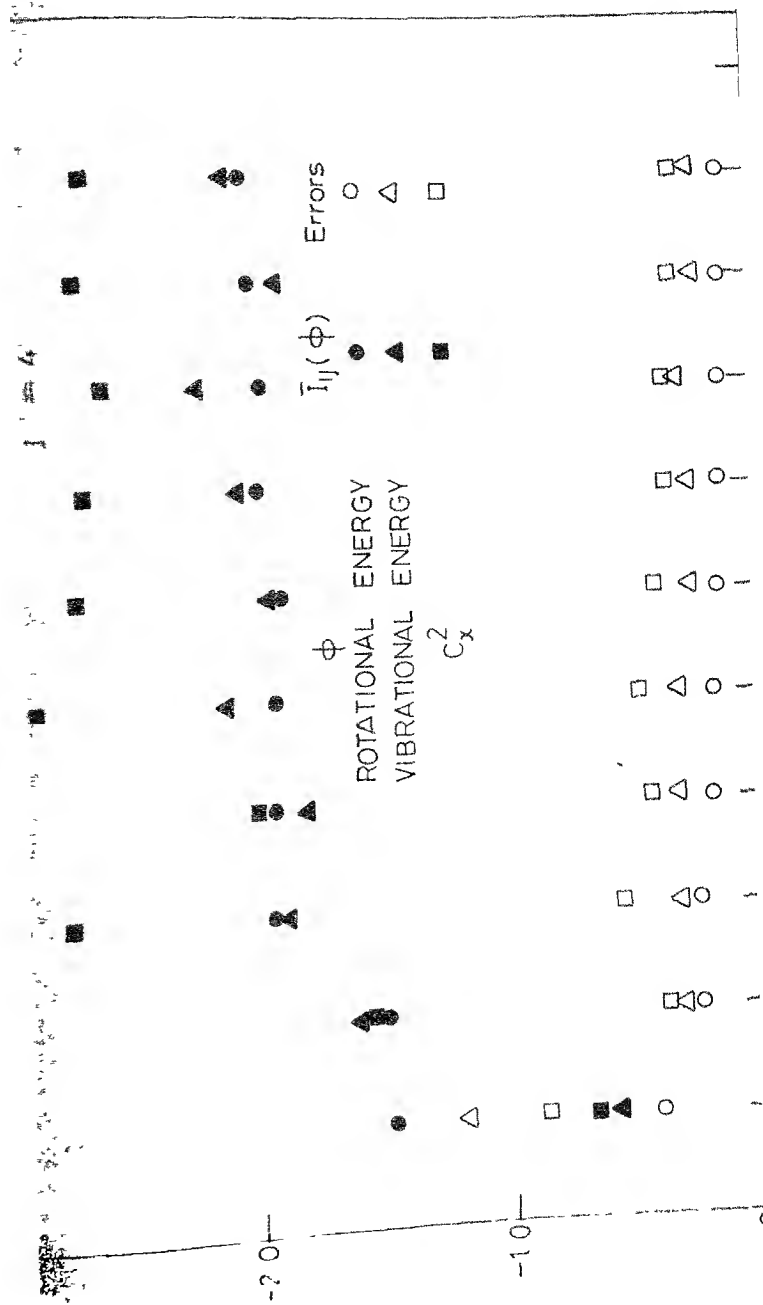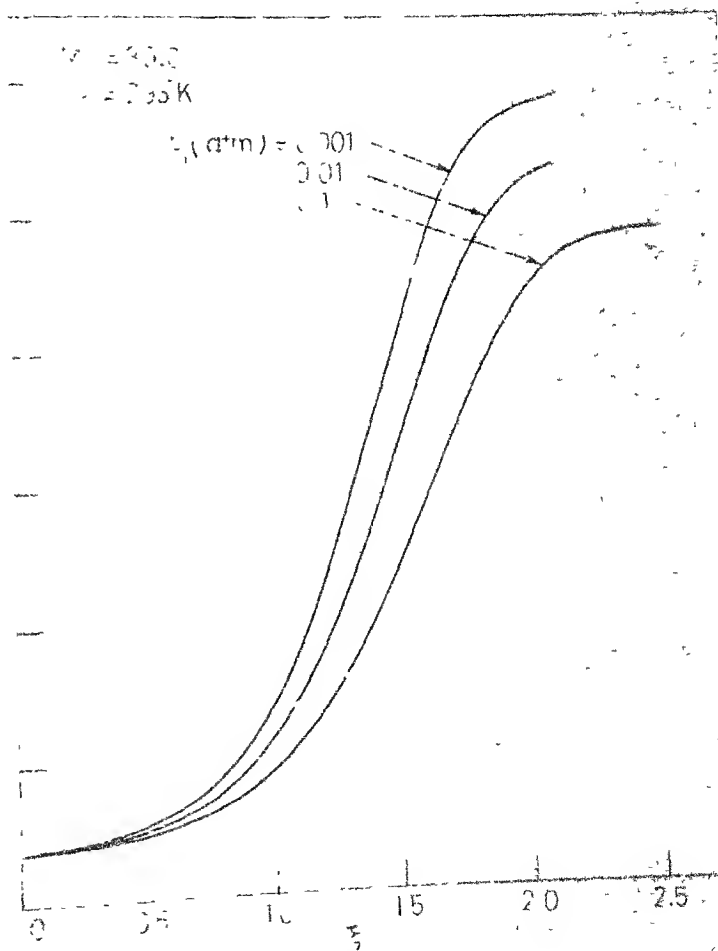
Errors

$\bar{I}_{IJ}(\phi)$

ROTATIONAL ENERGY

VIBRATIONAL ENERGY

ϕ

C_x^2

-20

-10

FIG. 7.1 DENSITY PROFILES FOR NITROGEN (KINETIC AL THEORY)

$M = 26.3$
$T_1 = 297$ $p_1(atm) - 0.01$
0.1
1

ξ

0.5   1.0   1.5   2.0   2.5   3.

FIG 71.2 DENSITY PROFILES FOR NITROGEN (TRIMODAL

δ

15.0

12.0

9.0

6.0

3.0

0.0

$M_1 = 20.0$
$T_1 = 293°\,K$

$P_i\,(atm) = 0.001$
         0.01
         0.1

$M_1 = 16.0$

$T_1 = 293°k$

$p(\text{atm}) = 0.001$
  0.01
  0.1
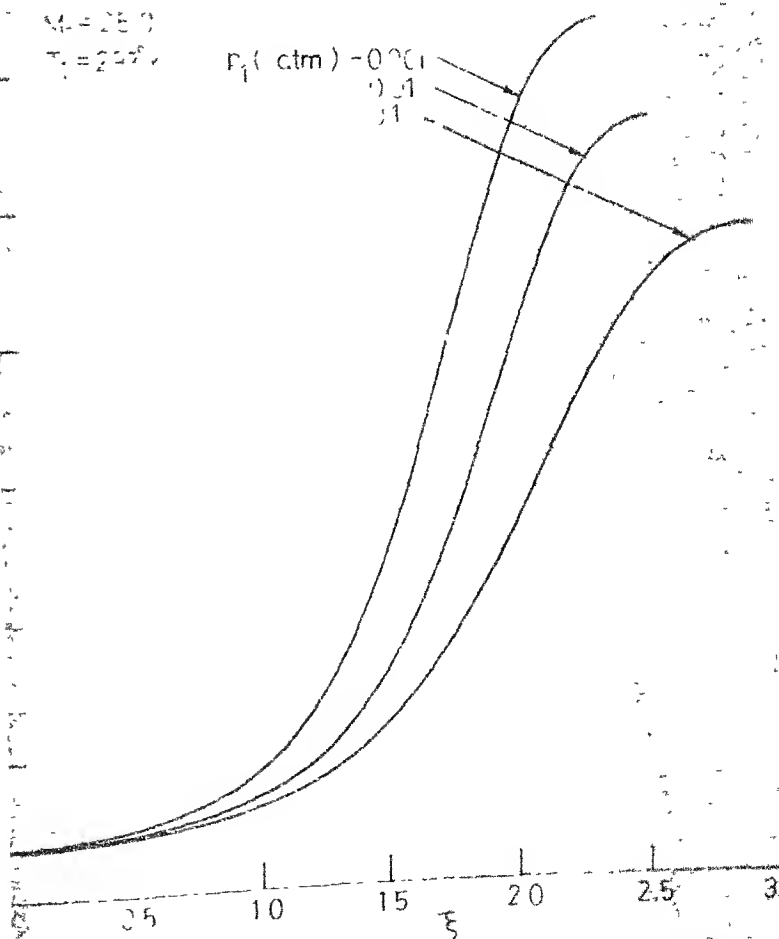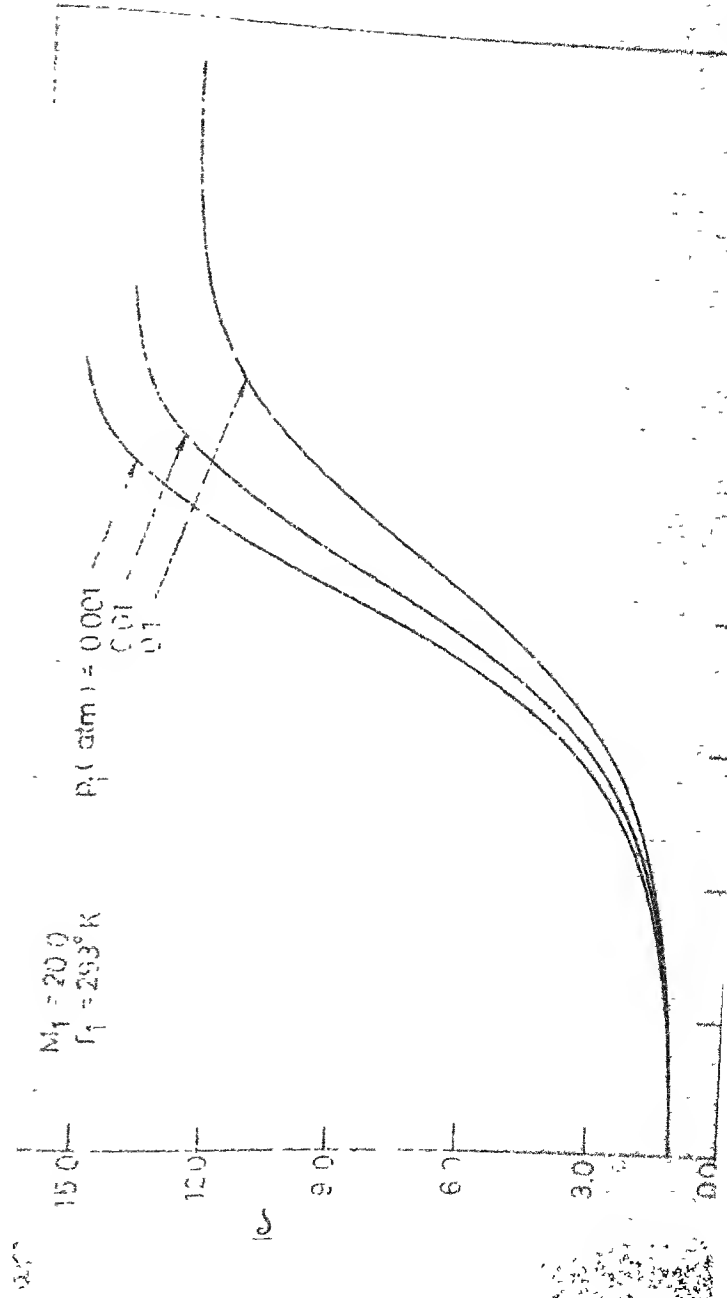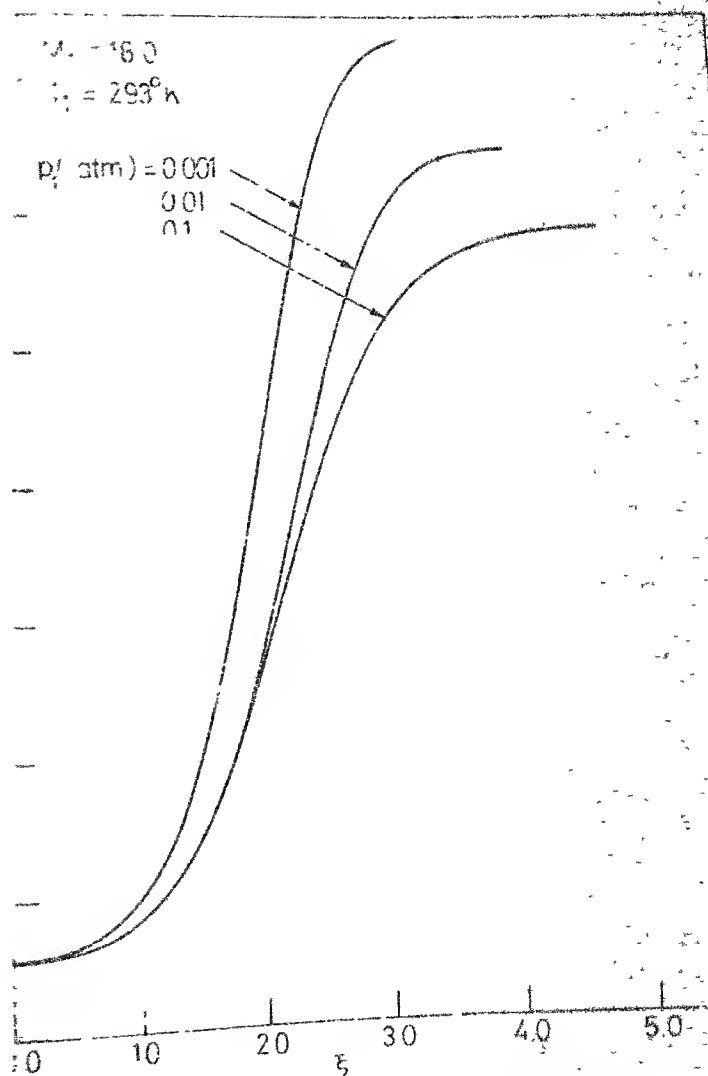
FIG 7.14 — DENSITY PROFILES FOR NITROGEN
(TRIMODAL THEORY)
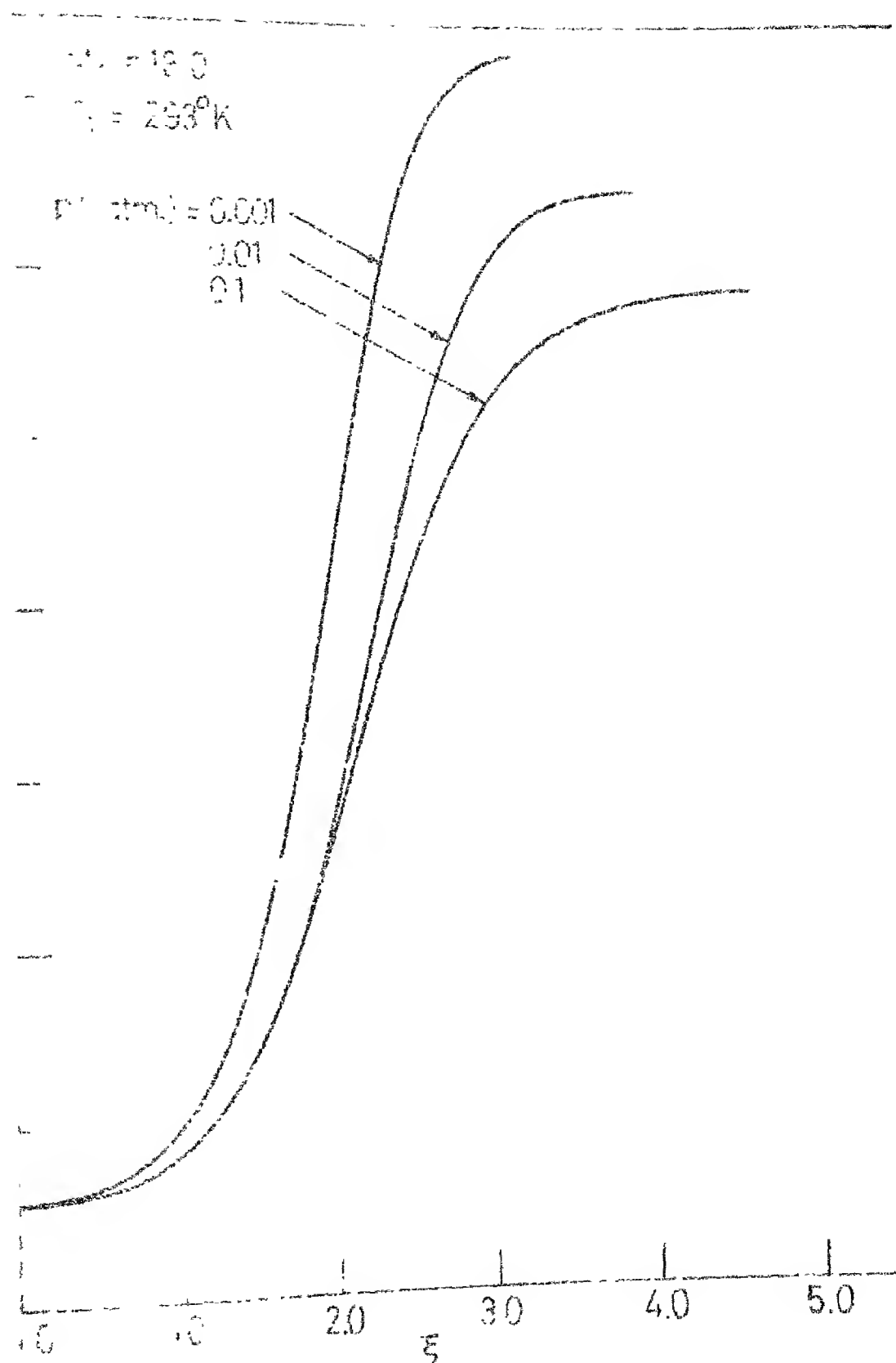
$M_1 = 18.0$

$T_1 = 293°K$

$P_1 (atm.) = 0.001$

0.01

0.1

ξ

1.0 2.0 3.0 4.0 5.0

FIG DENSITY PROFILES FOR NITROGEN
(BIMODAL THEORY)

$M_1 = 15.0$

$T_1 = 293°K$
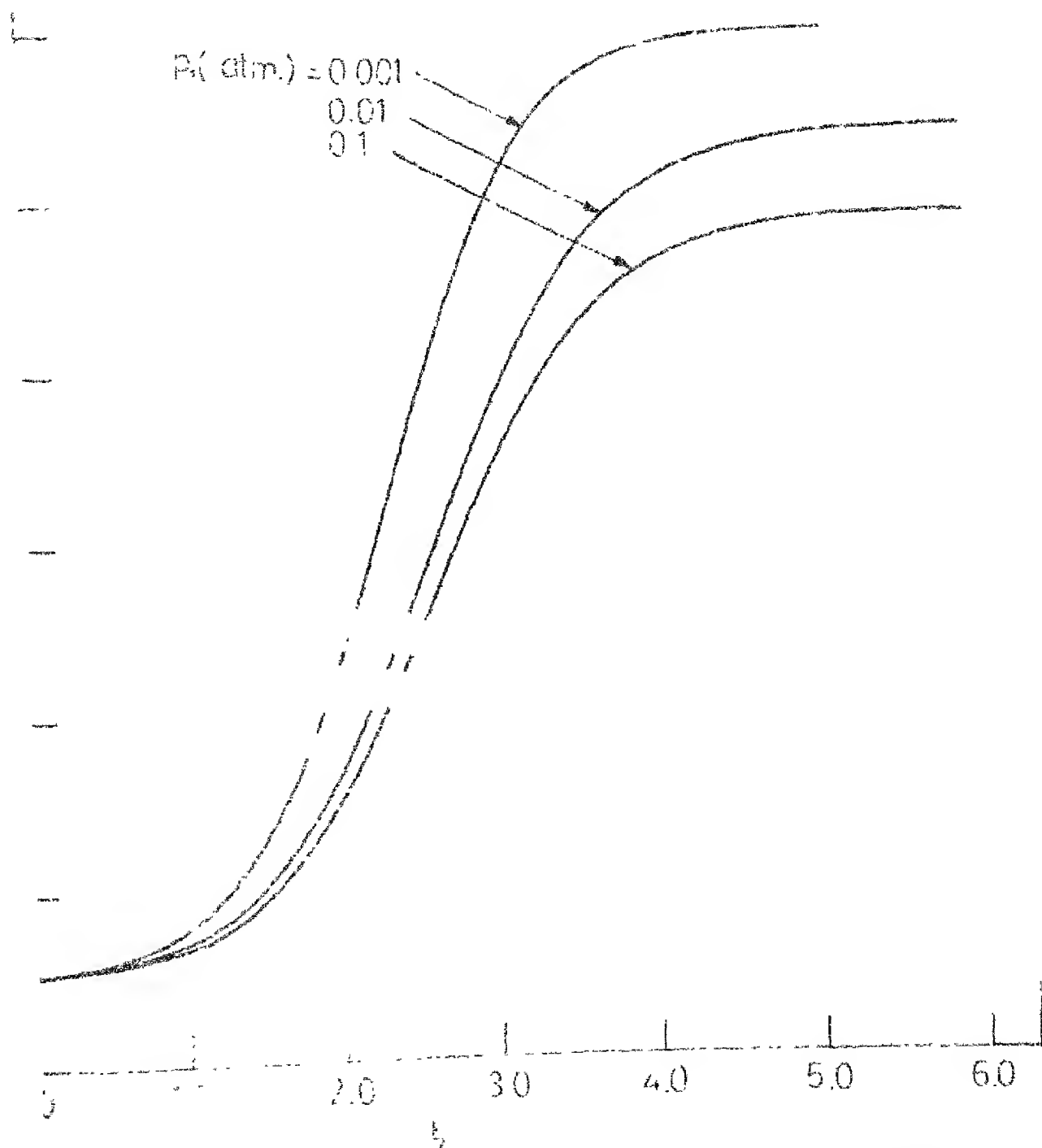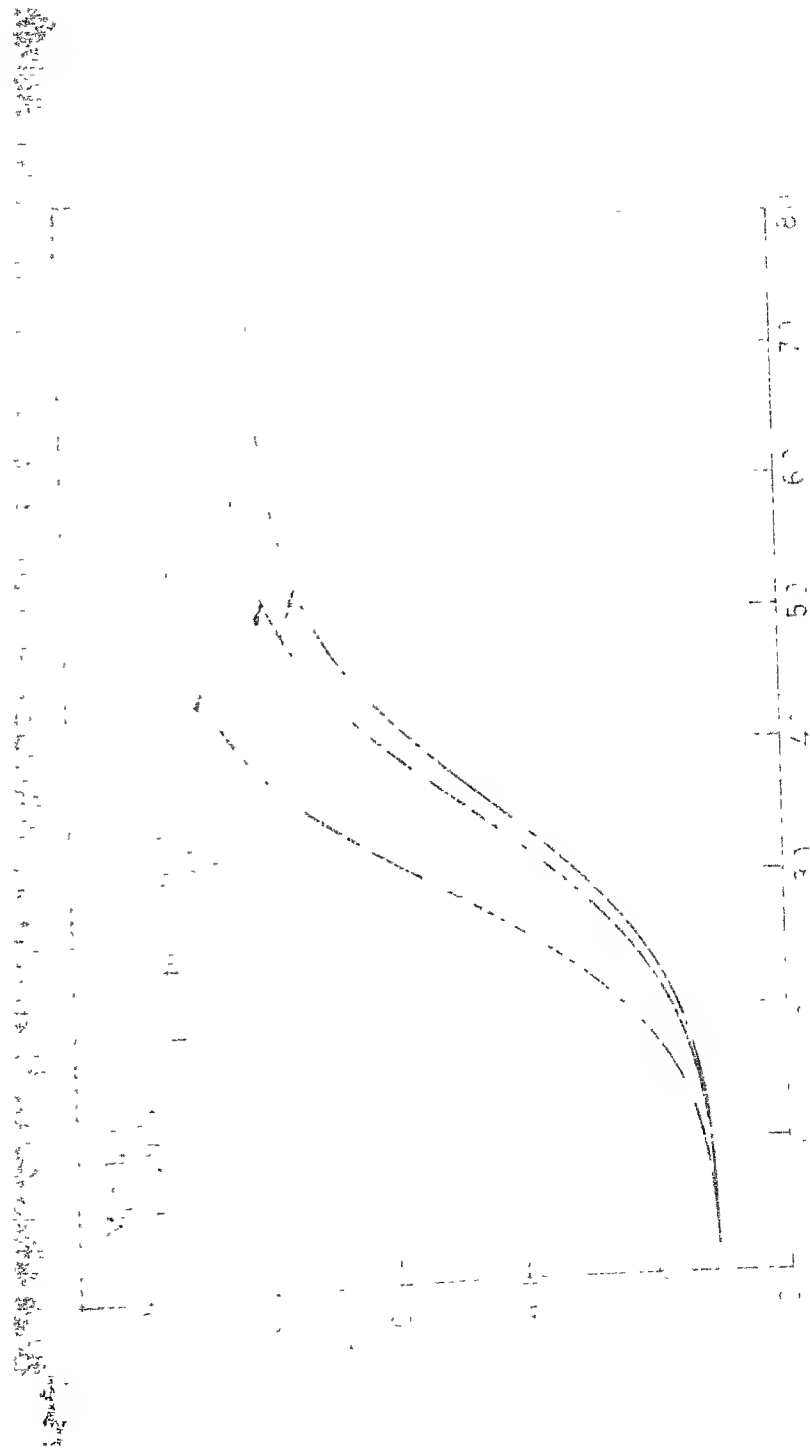
$P_1(atm.) = 0.001$

0.01

0.1

2.0   3.0   4.0   5.0   6.0

IG. 15. DENSITY PROFILES FOR NITROGEN (TRIMODAL TH

FIG. DENSITY OF HYDROGEN, THEORY

$M_1 = 11.0$
$T_1 = 293°K$

$p_1(atm) = .01$
.001
0.001

$\bar{T}_+$
$\bar{T}_H$
$\bar{T}_V$

TEMPERATURE PROFILES FOR NITROGEN
(IDEAL THEORY)

$M_1 = 25.0$
$T_1 = 293°K$

$P_1(\text{atm.}) = 0.1$ —————
$= 0.01$ — — —
$= 0.001$ — - — -

$\bar{T}_t$

$\bar{T}_{R_s}$

$\bar{T}_{V_s}$

ξ

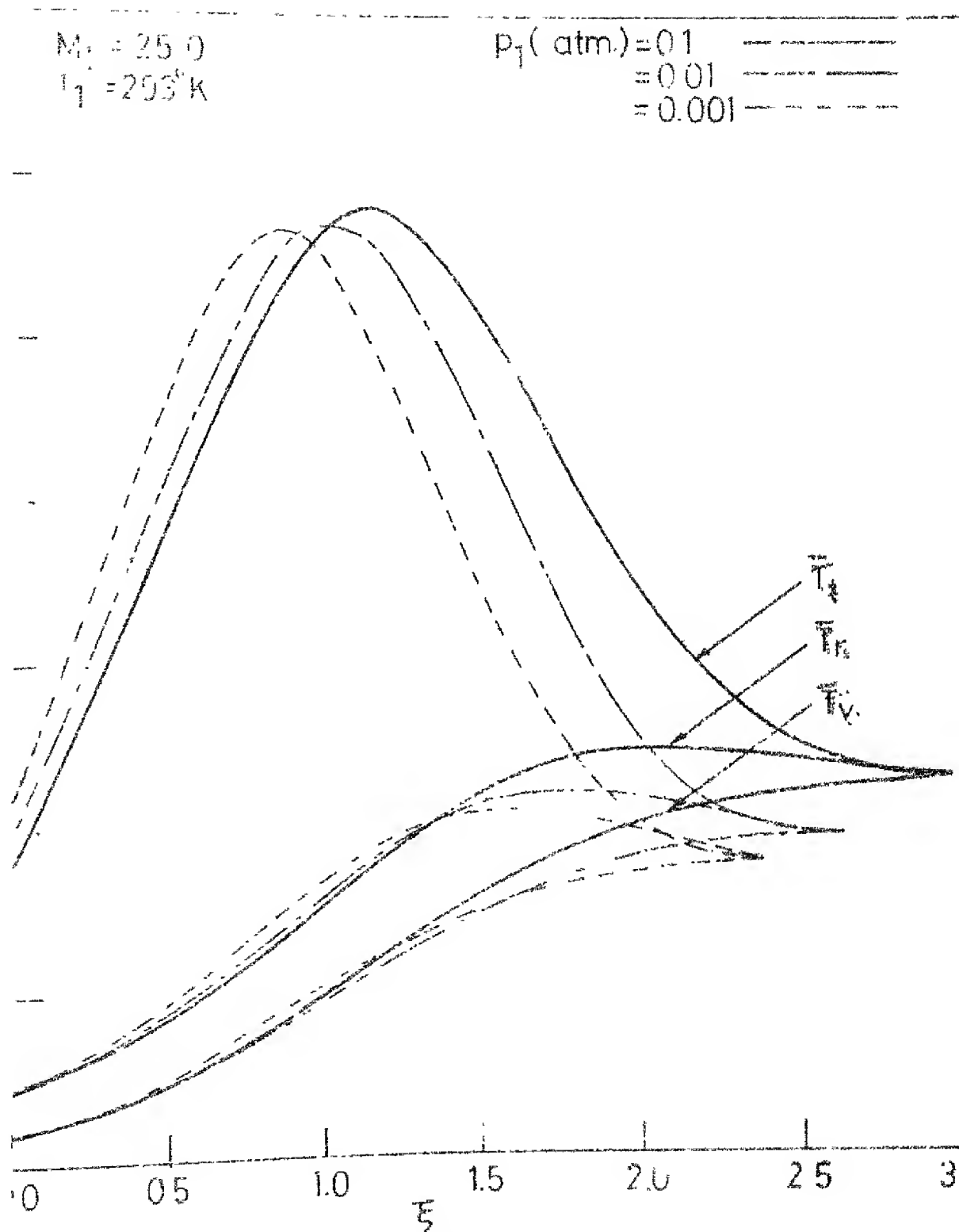'0   0.5   1.0   1.5   2.0   2.5   3
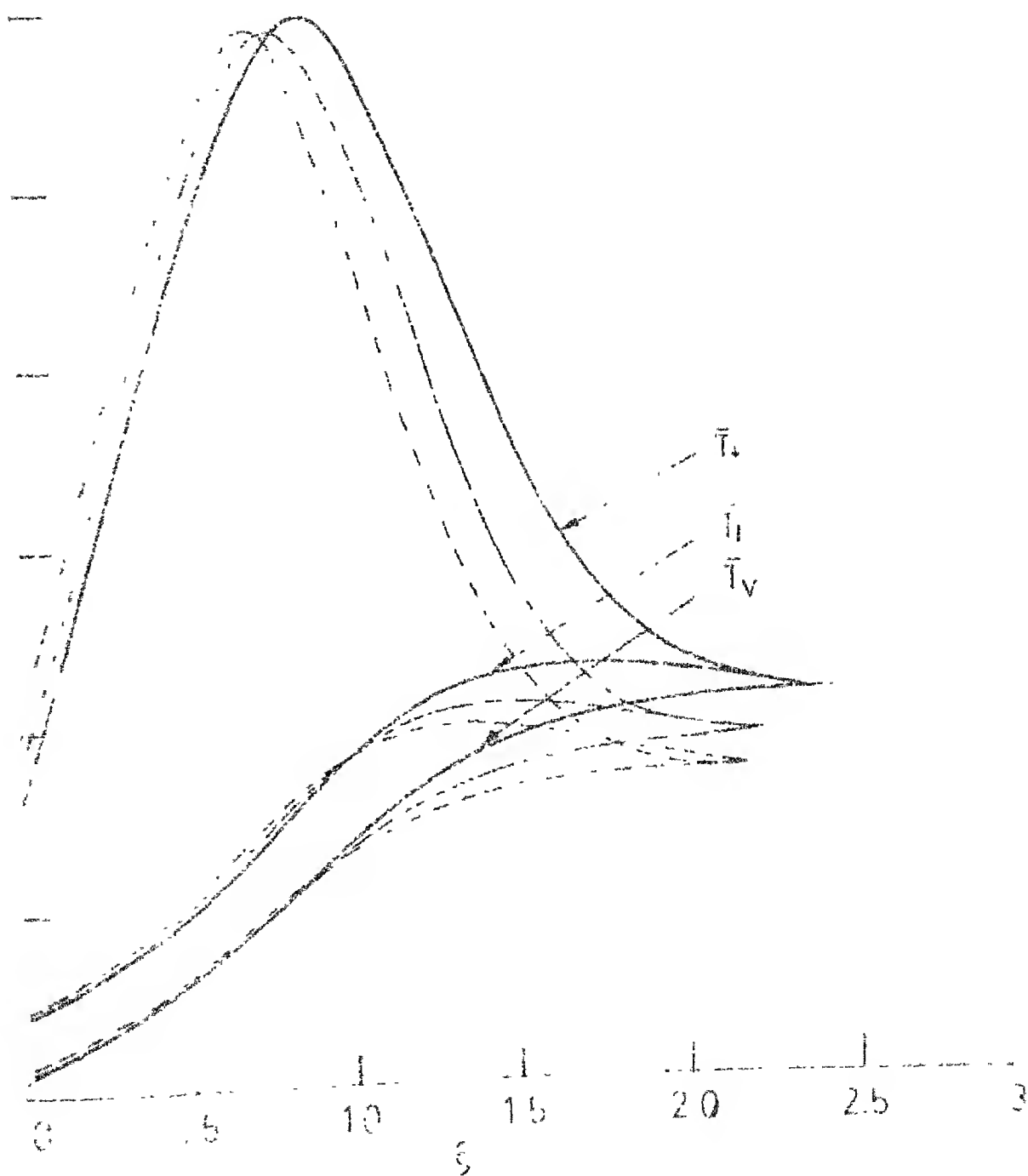
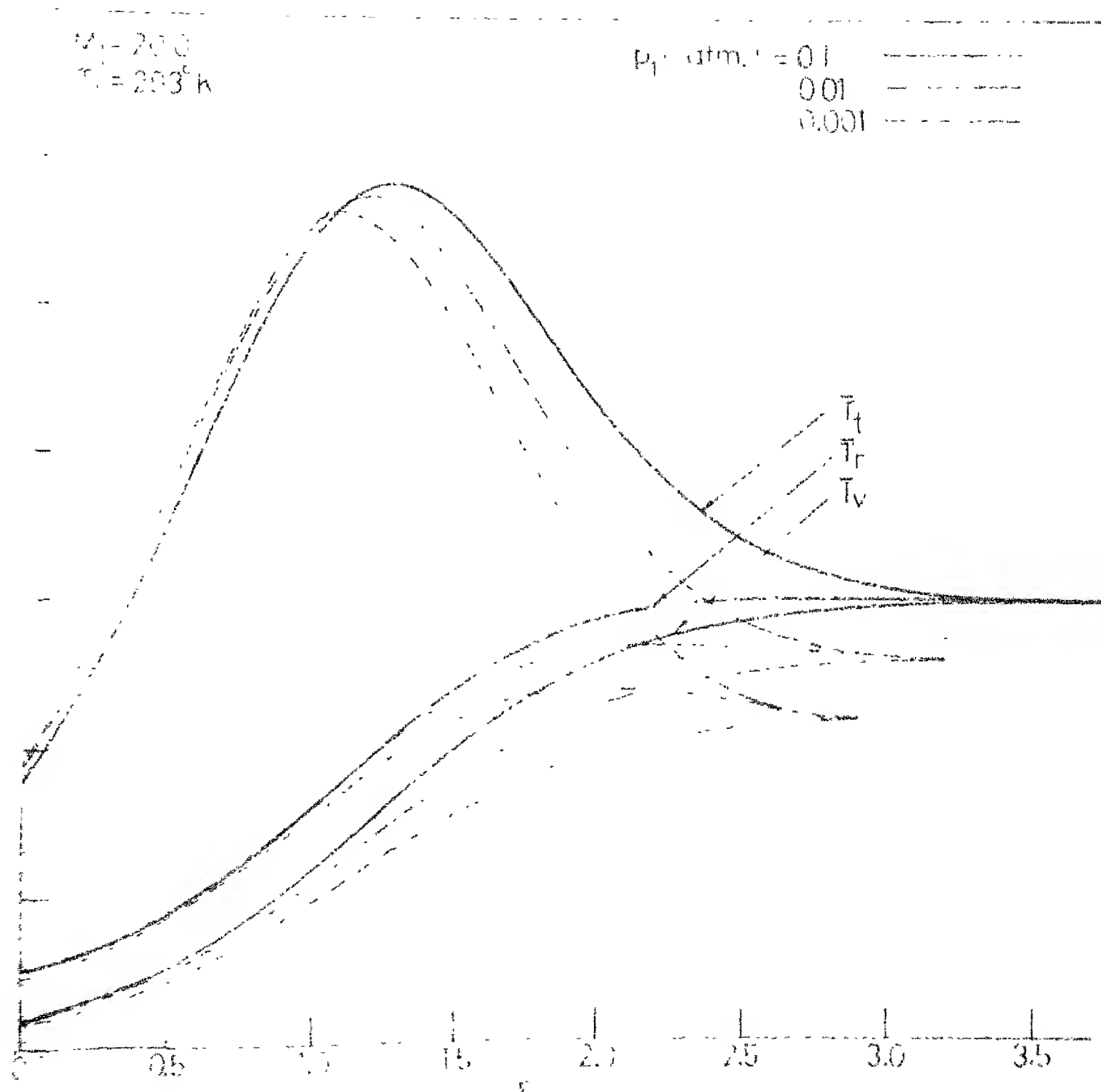FIG. 7.1.8 _ TEMPERATURE PROFILES FOR NITROGEN
(TRIMODAL THEORY)

FIG. 9. TEMPERATURE PROFILES FOR NITROGEN (TRIMODAL THEORY)